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March 12, 1999

Mr. William B. Baggett, Jr.
BAGGETT, MCCALL & BURGESS
3006 Country Club Road
Post Office Drawer 7820
Lake Charles, LA 70606-7820

RECEIVED MAR 16 1999

Re: Daniel J. and Elizabeth Elaine Ross v. Conoco, Inc., et al.
Our File No. 0177.2738708

Dear Mr. Baggett:

I am delivering herewith Minnesota Mining and Manufacturing Company's objections, comments, and response to the plaintiff's supplemental request for production of documents, together with copies of the documents.

By copy of this letter, I am notifying all defense attorneys that they may obtain copies of the documents by requesting them from me.

Sincerely,

Kevin J. Webb

Kevin J. Webb

KJW/sb
Enclosures
F:\27387\CORRES\Baggett17.doc
cc: All Counsel of Record

cc: Bill 3-17-99 KC
original Morris docs to Morris
1 copy of discovery

ELIZABETH ELAINE ROSS, ET AL.	*	14TH JUDICIAL DISTRICT COURT
VERSUS NO. 90-4837	*	PARISH OF CALCASIEU
CONOCO, INC., ET AL.	*	STATE OF LOUISIANA

MINNESOTA MINING AND MANUFACTURING COMPANY'S OBJECTIONS, COMMENTS, AND RESPONSES TO PLAINTIFFS' SUPPLEMENTAL REQUEST FOR PRODUCTION OF DOCUMENTS

Minnesota Mining and Manufacturing Company (3M) makes the following objections, comments, and responses to plaintiffs' supplemental request for production of documents:

GENERAL OBJECTIONS

3M makes the following general objections, which apply to all seven of the plaintiffs' supplemental requests for production:

Insofar as the plaintiffs' requests call for the production of documents that relate to any substance other than vinyl chloride, 3M objects because documents concerning any substance other than vinyl chloride are neither relevant nor reasonably calculated to lead to the discovery of admissible evidence.

3M objects to the requests for production on grounds that they seek to extend the time period for discovery beyond the period set forth by the court in its order of March 12, 1996. All of 3M's responses to the plaintiffs' requests for production are limited to the period 1973 through 1995 to conform with that order.

GENERAL COMMENTS

3M makes the following general comments, which apply to all sixteen of the plaintiffs' supplemental requests for production:

1. 3M makes this response to the plaintiffs' requests for production after a diligent search of its records This search is continuing. 3M reserves the right to supplement its response should it discover additional documents which may be responsive to the plaintiffs' request for production.

2. Certain of the documents produced herewith may be responsive to more than one of the plaintiffs' numbered requests.

3 3M has assigned production numbers to the documents which are being produced herewith The production numbers assigned by 3M and the individual numbered request or requests to which 3M believes them to be responsive are:

3M Document Nos.	Responsive to Request No.
3M 110285 - 3M 110291 3M 110293 – 3M 110317 3M 110320 – 3M 110341 3M 110366 – 3M 110375 3M 110387 – 3M 110390 3M 110398 – 3M 110435	1 & 2
3M 010111 – 3M 010112 3M 010523 – 3M 010526 3M 105130 – 3M 105132 3M 105169 – 3M 105175 3M 105183 – 3M 105185 3M 105723 – 3M 105727 3M 107458 – 3M 107459 3M 107462 3M 107467 – 3M 107469 3M 109721 – 3M 109732 3M 110436 – 3M 110457 3M 110469 – 3M 110488 3M 110497 – 3M 110524 3M 110542 – 3M 110643 3M 110648 – 3M 110667 3M 110669 – 3M 110674 3M 110697 – 3M 110713 3M 110725 – 3M 110737 3M 110754 – 3M 110778 3M 110809 – 3M 110929 3M 111007 – 3M 111107	3
3M 110398 – 3M 110435 3M 110930 – 3M 110966	4 & 5
No Responsive Documents	6 & 7

RESPONSES AND SPECIFIC OBJECTIONS

3M makes the following responses and/or specific objections to the plaintiffs' supplemental requests for production:

REQUEST FOR PRODUCTION NO. 1:

Please produce any notes, memorandum, correspondence, record, minutes of meetings, calendar entries, and any other documents with regards to the ISEA (Industrial Safety Equipment Association) and passive dosimeters for any employee and/or officers of 3M, including but not limited to, Bob Weber and James Kvickstad.

RESPONSE TO REQUEST FOR PRODUCTION NO. 1:

See comment No. 3 above

REQUEST FOR PRODUCTION NO. 2:

Please produce any correspondence, telephone message slips, telephone conversation summaries, or any other documents with regards to the ISEA (Industrial Safety Equipment Association) and passive dosimeters for any employee and/or officers of 3M, including but not limited to, Bob Weber and James Kvickstad.

RESPONSE TO REQUEST FOR PRODUCTION NO. 2:

See comment No. 3 above

REQUEST FOR PRODUCTION NO. 3:

Please produce any written or electronic record, including e-mail, which in any way concerns passive dosimeters and vinyl chloride and/or halogenated hydrocarbons and/or chlorinated hydrocarbons.

RESPONSE TO REQUEST FOR PRODUCTION NO. 3:

For written or electronic records that pertain to passive dosimeters and vinyl chloride, please see the documents produced by 3M in its response to the plaintiffs' original request for production.

Insofar as the request seeks written or electronic records that pertain to passive dosimeters and any other halogenated or chlorinated hydrocarbons, 3M objects to the request on grounds that it is too broad, vague and general to be susceptible of a categorical response, calls for information which is not admissible or reasonably calculated to lead to the discovery of the admissible evidence, and cannot be answered without imposing undue hardship and expense upon Minnesota Mining and Manufacturing Company. Without waiving those objections, 3M responds to the request as follows:

See comment to No. 3 above.

REQUEST FOR PRODUCTION NO. 4:

Please produce any notes, memorandum, correspondence, record, minutes of meetings, calendar entries, and any other documents with regards to the SEI (Safety Equipment Institute) and passive dosimeters.

RESPONSE TO REQUEST FOR PRODUCTION NO. 4:

See comment No. 3 above

REQUEST FOR PRODUCTION NO. 5:

Please produce any correspondence, telephone message slips, telephone conversation summaries, or any other documents with regards to the SEI (Safety Equipment Institute) and passive dosimeters.

RESPONSE TO REQUEST FOR PRODUCTION NO. 5:

See comment No. 3 above

REQUEST FOR PRODUCTION NO. 6:

Please produce any notes, memorandum, correspondence, record, minutes of meetings, calendar entries, and any other documents with regards to the ASTM Committee D22 on Sampling and Analysis of Atmospheres (including but not limited to Subcommittee designation D22.04 on Methods of Sampling and Analysis of Work Place Atmospheres).

RESPONSE TO REQUEST FOR PRODUCTION NO. 6:

None.

REQUEST FOR PRODUCTION NO. 7:

Please produce any correspondence, telephone message slips, telephone conversation summaries, or any other documents with regards to the ASTM Committee D22 on Sampling and Analysis of Atmospheres (including but not limited to Subcommittee designation D22.04 on Methods of Sampling and Analysis of Work Place Atmospheres).

RESPONSE TO REQUEST FOR PRODUCTION NO. 7:

None.

Kevin J. Webb (#17857)
Henderson, Hanemann & Morris
A Professional Law Corporation
300 Lafayette Street
Houma, LA 70360
Tel: (504) 868-2081
Attorneys for Minnesota Mining
and Manufacturing Company

CERTIFICATE

I HEREBY CERTIFY that a copy of the above and foregoing has this day been forwarded to all known counsel of record by placing same in the United States mail, postage prepaid and properly addressed.

Houma, Louisiana, this 12th day of March, 1999.

F:\27387\PLD\Req. for Prod.doc

Kevin J. Webb

Internal Correspondence

3M

Occupational Health and Envtronmental Safety Division

To: R.J. Haggerty - OH&ESD - 275-6W-01

From: R.A. Weber (7-4459) - OH&ESD - 260-3B-09

Subject: **ISEA MEETING ON DIFFUSION MONITORS**

Date: February 14, 1995

BACKGROUND

OSHA has requested ISEA to write a validation procedure for diffusion monitors. OSHA representative Bob Curtis indicated that OSHA wants employers to take a more proactive approach to workplace assessments. OSHA believes that if diffusion monitors could be officially validated, employers would more likely perform workplace assessments.

Members of the ISEA Gas & Vapor Detection Committee are going to write a Diffusion Monitor Validation Protocol. The protocol will be forwarded to ANSI and ANSI will adopt it as a standard. SEI, a certification branch of ISEA will then use the ANSI standard for their certification process.

MEETING HIGHLIGHTS

On January 26 and 27, ISEA members, OSHA and other interested parties met to discuss the development of the standard. The following people were in attendance:

Bill Erny (ISEA)
Gus Manning (Assay Tech)
Marshal Parker (Clayton)
Katie Spear (MSA)
Ralph Burns (Neotronics)
Martin Harper (SKC)
Rob Roberson (Sensidyne)
Victor Elia (National Paper)
Skip Elliott (Envirometrics)
Alan Ilaid (Pro-Tech)
Bob Curtis (OSHA)
Rick Lee (OSHA)
Warren Hendricks (OSHA)

The goals of the standard are to define performance criteria, develop testing requirements, define terminology and labeling, and finally allow manufacturers flexibility in defining the limits of their diffusion monitors.

The committee attempted to define what types of diffusion monitors should be covered by the standard. There was much discussion if electrochemical sensors should be included. It was agreed that for the time being, these types of devices should be excluded because they have unique performance requirements. However, it was agreed that passive direct reading electrochemical air monitors would eventually be part of the standard. Therefore, this standard will not only impact our present line of diffusion monitors, it could also impact our sensor program.

We discussed standards that were in existence today that could be used as the starting point for the ANSI document. The performance criteria (i.e., reverse diffusion, capacity, sampling rate etc...) outlined in the NIOSH and CEN documents are the same and the committee agreed that we should include them in our document. Although we agreed on the performance criteria, we did not agree with the test methods that NIOSH and CEN used to evaluate the performance criteria. SKC representative, Martin Harper, presented their modified NIOSH protocol. The SKC protocol included the same performance criteria, however, they modified some of the evaluation procedures. Martin indicated SKC has spent a lot of time and money to validate their monitors according to the NIOSH procedure and at this time, they are not willing to spend more time and money on validating their monitors to a new ANSI standard.

I indicated that 3M has just developed their own validation protocol that is a hybrid between the NIOSH and CEN documents and that we will be presenting our views at the AIHC&E. I will be forwarding the protocol to committee members for review as a possible starting point for the ANSI standard.

SUMMARY AND COMMENTS

One of the major reasons why the diffusion monitors market never reached its projected size is because OSHA never officially recognized diffusion monitors as a valid sampling device. With the new OSHA exposure assessment standard, OSHA

officials are asking employers to better characterize their workplace by taking more samples on a routine basis. In fact, Bob Curtis indicated that OSHA will be citing more and more people for lack of sampling data. Bob also indicated that if OSHA expects employers to routinely monitor their workplace, they will need a simple, easy-to-use sampling device, like the diffusion monitor.

OSHA commitment to this program is indicated by their newly approved protocol for evaluation of direct reading passive monitors (see insert). SEI is going to adopt this protocol as an interim standard for certification. The new ANSI standard that we are developing will then replace this interim standard.

In my opinion, this ANSI standard plus the recognition and support by OSHA will help grow the diffusion monitor market not only here in the U.S., but also around the world.

This is an exciting time and a great opportunity for diffusion monitors and I feel that we should take advantage of this opportunity. We need to continue our leadership position.

Our next committee meeting will be in 2 to 3 months.

RAW:llj/9
Attachment
cc: R.A. Bernier - OH&ESD - 76-2E-02
D.C. Breckle - OH&ESD - 275-6W-01
A.R. Johnston - OH&ESD - 260-3B-09
R.E. King - OH&ESD - 260-3B-09
D.J. Larsen - OH&ESD - 260-3B-08
A.C. Murray - OH&ESD - 275-6W-01
J.B. Palazzotto - OH&ESD - 260-3B-08
K.E. Reed - OH&ESD - 260-3A-02
Y.T. Shih - OH&ESD - 260-3B-08
G.H. Smith - OH&ESD - 275-6W-01
L.G. Swope - OH&ESD - 275-6W-01
D.P. Wilmes - OH&ESD - 260-3A-07

Internal Correspondence

3M

Occupational Health and Environmental Safety Division

To: R.J. Haggerty - OH&ESD - 275-6W-01
R.E. King - OH&ESD - 260-3B-09

From: R.A. Weber (7-4459) - OH&ESD - 260-3B-09

Subject: **ISEA INSTRUMENT & GROUP MEETINGS**

Date: June 2, 1995

The ISEA Instrument group had two meetings during the AIHC. The first meeting involved the subcommittee working on the diffusion monitor protocol and the second was the entire instrument group.

Review of Diffusion Monitor Subcommittee Meeting

The following people were in attendance: Skip Elliott - Environmetrics, Gus Manning - Assay Technology, Lawrence Locker - Advanced Chemical Sensors, Katie Spear - MSA, Bob Curtis - OSHA, Martin Harper - SKC, Stephen Zlocysti - MSA (Auer).

The group elected officers; Skip Elliott was elected chairman and I was elected vice-chairman.

Stephen Zlocysti, chairman of the CEN committee working on the European diffusion monitor standard gave our group an update on their standard prEN838. This standard is now out for votes and he expected it to be a final standard by the end of the year.

Since our last meeting in February, the group has been very active in writing the standard. We reviewed the draft document during this session and in general, we had some lively discussions. Some of the issues involved the following:

1. The types of devices that this standard should cover. Presently, we have settled on three classifications.

2. We discussed the evaluation criteria and we ended up with a consensus on what types of tests need to be conducted. Specifics on sample sizes and testing levels are still open for further discussion. We agreed that we will not include pressure in evaluation criteria and we also agreed that factorial designed experiments may be run as an option.

3. We agreed that the document should contain language or guidance on field evaluations.

4. The document will contain recommendations for manufacturers. This section will include information on quality control programs and labeling.

5. We decided that ±25% accuracy would not be a requirement. Accuracies only need to be determined and started.

Each member of the committee has specific sections to develop. Draft sections need to be submitted by the end of July. In August the document will be sent out for committee review. If committee finds this draft acceptable, we will then distribute to a field of experts for their comments. These comments will then be reviewed at our next committee meeting. We are scheduled to meet again during the National Safety Congress.

Instrument Group Meeting

The members of this group are mainly concerned about direct reading instruments. All of the major players in the business are participants in ISEA. Following is a list of items that the committee is actively involved with: ANSI Standard on Detector Tubes, ISA O_2 Standard, NFPA306, CEN Instrument Standards, ANSI Z-117 Confined Space Standard, OSHA 1910.134 and writing an ANSI Diffusion Monitor Protocol.

Although we presently do not have a product that fits into the direct reading sensor market, the meeting gave me an understanding of issues that our competition is dealing with.

Summary

I walked away from this meeting realizing that there is a maze of instrument and sensor standards that we need to better understand if we ever plan to enter this market. My major objectives in working with this ISEA committee is to assist in writing the ANSI Diffusion Monitor Protocol and to learn about the standards and issues of gas and vapor detection instruments.

RAW:llj/45
cc: D.C. Breckle - OH&ESD - 275-6W-01
A.R. Johnston - OH&ESD - 260-3B-09
L.A. Koerschner - OH&ESD - 260-3B-10
D.J. Larsen - OH&ESD - 260-3B-08
A.C. Murray - OH&ESD - 275-6W-01
J.B. Palazzotto - OH&ESD - 260-3B-08
K.E. Reed - OH&ESD - 260-3A-02
Y.T. Shih - OH&ESD - 260-3B-08
L.G. Swope - OH&ESD - 275-6W-01

Industrial Safety Equipment Association

MINUTES
Passive Dosimeter Manufacturers Meeting
Thursday, January 26, 1995, and
Friday, January 27, 1995
Doubletree Hotel
Salt Lake City, UT

PRESENT

Bob Weber	3M Company
Larry Locker	Advanced Chemical Sensors Company
Gus Manning	Assay Technology
Marshall Parker	Clayton Environmental
Skip Elliott	Environmetrics Products
William Erny	Industrial Safety Equipment Association
Katie Spear	Mine Safety Appliances Company
Victor Elia	NCASI
Ralph Burns	Neotronics
Bob Curtis	Occupational Safety and Health Administration
Rick Cee	Occupational Safety and Health Administration
Warren Hendricks	Occupational Safety and Health Administration
Allan Aylward	Pro-Tek
Ron Roberson	Sensidyne Inc.
Martin Harper	SKC

1. CALL TO ORDER

The meeting was called to order at 9:10 a.m.

2. INTRODUCTIONS AND ROLL CALL

As the first order of business, each participant introduced himself and explain his interest in the standards development program for passive monitors. A common interest was expressed by the manufacturers in supporting and participating in the development of standard requirements for passive monitors. OSHA explained that through the establishment of a reliable validation method, they could more readily consider the use of passive monitors by OSHA field compliance officers in obtaining a broader range of exposure data, providing a better characterization of workplace exposure. Bill Erny gave a brief presentation on the ISEA. Bill explained that ISEA is the leading national association of personal protective equipment manufacturers and is organized into the following thirteen product group categories:

- Clean Room
- Eye and Face Protection
- Flammable Containers
- Emergency Eyewash and Shower
- Fall Protection
- Industrial First Aid

- Industrial Warning Devices
- Head Protection
- Respiratory Protection
- Safety Wearing Apparel
- Instruments
- Hearing Protection
- Respiratory Protective Escape Devices

The mission of the ISEA is to support its members in manufacturing and marketing the highest quality products to protect the safety and health of workers. ISEA does this by:

- acting as the industry voice
- promoting standardization of personal safety products
- representing the industry before government bodies
- providing timely information to members for use in making important business decisions
- promoting the proper use of PPE as essential to worker safety and health
- providing a forum for members to meet and discuss common industry-related issues

Bill Erny explained that as an American National Standards Institute (ANSI) accredited standards developer, ISEA provides a forum for manufacturers to develop product performance standards through the ANSI program.

Bill Erny reported that ANSI has given a verbal "green light" for ISEA to initiate a standards program for passive monitors. When initiated, ANSI which will announce the project in its "Standards Action" publication requesting public comment and interested parties who wish to be included on the review list.

Bill Erny explained the requirements of participants and noted that this would be the last meeting as an open forum. All future meetings will be open to ISEA members and eligible participants only. ISEA will send a membership ballot to interested parties before March 1. Others industry experts may be invited to participate at the discretion of the Committee including non-manufacturers who have been identified as having significant knowledge and experience in the field of interest and who would significantly add value to the standards program.

Manufacturers who choose not to join the ISEA but wish to participate in the standards development program may do so on a per meeting basis and are charged a per meeting fee of $375.00 to help cover meeting expenses and administrative costs. In addition, non-ISEA member participants are required to share in project expenses incurred during the course of work, such as the purchase of technical documentation and the conducting of testing programs. Eligible non-member participants can vote on committee meeting issues but not on ISEA issues including the final approval of the standard for submission to ANSI.

3. PRODUCT CERTIFICATION

Martin Harper reported on the recent establishment of an ASTM workplace atmosphere program, D2206, chaired by Richard Deanchick of Alcoa. NIOSH representatives Dave Barly and Gene Kennedy are participating. It was suggested that a possible joint venture program between ANSI and ASTM should be explored. Bill Erny was requested to contact ASTM and NIOSH to research the issue further and report back to the committee at the next meeting.

The attached news release, published in the *SEI Update*, was distributed to participants announcing the approval by the SEI Board of Directors to initiate a certification program for direct reading passive monitors. SEI will use an OSHA reviewed/ modified NIOSH protocol to conduct certification testing. When complete SEI would adopt the ANSI standard. Attached is the letter from OSHA to SEI regarding OSHAs review of the SEI protocol. Bob Curtis noted that OSHA expects to consider SEI-certified passive monitors for use by OSHA field officers by March 1.

4. PASSIVE MONITOR STANDARDS DEVELOPMENT PROGRAM

The Group discussed the need for standardization. It was stated that standardization is required to provide product credibility by establishing a consistently reproducible test procedure to verify a product's performance as claimed by the manufacturer. The following goals of the standards program were identified:

- to facilitate the characterization of workplace exposures
- to provide accurate information to users
- to establish minimum performance based criteria
- to establish standardized test conditions and test methods for product evaluation
- to validate a manufacturer's claims
- to encourage innovation
- to encourage multiple suppliers/competition
- to standardize terminology and facilitate understanding

The scope of the standard was discussed, including the consideration of electro-chemical sensor technology. The Group noted the wide differences between the two technologies and the resulting differences in the appropriate evaluation methods that would need to be developed. The Group concluded that electro-chemical sensors will not be considered at this time but could be added later. Furthermore, the Group concluded that the following types of technology will be excluded from this project at this time:

- electro-chemical sensors
- direct reading short-term color tubes
- length of stain-pump required (active)

As a result, the Group developed the following scope of technologies to be included under the ISEA passive monitor standards program:

- passive monitoring devices--no active pump required--diffusive sampler
- no user calibration required
- Type A--Direct Reading/Color Change (field analysis assay)
- Type B--Laboratory analysis

The following suggested elements to include in the standard were identified:

- laboratory requirements/accreditation
- criteria for extrapolation to similar compounds
- manufacturer's statement of effective operating ranges
- accuracy limits versus validation manufacturers' claims

- Q.A. program requirements
- manufacturers product use instructions/limitations--standardized presentation of information
- re-test requirements--changes to form, fit, or function
- specify compounds tested to
- tolerances on testing conditions (ΔT)
- test orientation
- test apparatus specifications--reference test methods in Appendix
- separate PEL and STEL tests

The Group discussed the potential to include criteria for extrapolation of test data to similar compounds. It was suggested that a peer-review group could be established to evaluate and approve a manufacturer's request for extrapolation. The manufacturer would be required to submit justification and rationale. The peer-review group could be established as an ANSI standing committee or as a part of a certification program.

It was discussed that an accuracy requirement of 25% is established by the NIOSH protocol. It was noted that the significance of accuracy depends greatly on the application and levels of exposure. It was recommended that that accuracy may be better driven by market forces rather than through mandated requirements. At this time, the Group determined that accuracy requirements may not be needed, but should be re-addressed at a later date.

Requirements for Type B, laboratory analyzed monitors, were discussed. It was suggested that laboratory performance requirements should be included within the standard. Two different approaches were suggested: (1) Spell out specific laboratory requirements; or (2) require laboratory accreditation. The group determined that more discussion was needed on this issue.

The Group identified the following suggested performance criteria to be included into the standard:

- analytical recovery
- reverse diffusion
- face velocity/wind effects
- factorial
- detection limit
- rate and capacity
- storage stability/shelf life
- temperature effects
- accuracy/precision

The following "parked issues" were identified:

- ANSI versus ASTM/ANSI joint program
- list of standards reviewers/list of canvasses
- industry experts
- involvement of NIOSH/EPA/MSHA
- define a minimum performance level (box) or verify a manufacturer's claims
- statement of product limitations
- specific quality assurance requirements
- third-party certification
- extent of test apparatus specifications and reference methods

The following suggested format was developed:

Section Number	Heading
I	Introduction
II	Scope and Purpose
III	Definitions of Terms
IV	Classification
V	Technical Parameters
VI	Extrapolation Criteria
VII	Truth in Labeling

The following action items were assigned:

Section I--Gus Manning, Katie Spear, and Bob Curtis
Section II--Skip Elliott, Rich Cee
Section II--Skip Elliott, Martin Harper, Rich Cee
Section IV--Martin Harper
Section V--Gus Manning, Katie Spear

Bill Erny was assigned to research ANSI requirements for the use of draft standards and inquire the level of interest of NIOSH/EPA. Martin Harper was assigned to inquire into the level of interest of the following user groups:

- Dupont
- Romm and Haas
- Chevron
- Exxon
- Shell

5. OTHER BUSINESS

Bob Weber expressed his interest in acting as Committee chairman. Committee members will be requested to vote on this issue at the next meeting.

6. NEXT MEETING

The next meeting was scheduled in accordance with the ISEA Instruments Group meeting in conjunction with the American Industrial Hygiene Conference and Exposition (AICHE) in Kansas City, Mo., on May 21. More specific details regarding the meeting place and time will be announced at a later date.

7. ADJOURNMENT

There being no further business to come before the meeting, a motion to adjourn was adopted at 12:35 p.m.

Respectfully submitted,

William J. Erny
Manager of Product Groups

ISEA Industrial Safety Equipment Association

MINUTES

Passive Monitor Standards Committee
of the
Instruments Group
Sunday, May 21, 1995
Kansas City Marriott

ISEA MEMBERS PRESENT

Envirometrics Products Co.	Skip Elliott
3M Company	Bob Weber
Mine Safety Appliances	Katie Spear

OTHERS PRESENT

Advanced Chemical Sensors	Laurence D. Locker
Advanced Chemical Sensors	Hannah Johnson
Assay Technology	Gus Manning
Auergesellschaft/Germany	Stefan Zloczysti
Clayton Environmental	Marshall Parker
Dow Chemical Company	Rolf M.A. Hahne
OSHA/SLTC	Bob Curtis
SKC Inc	Martin Harper
SKC Inc	Lloyd Guild
Webster, Chamberlain & Bean	David Goch
ISEA	Bill Erny

PRESIDING — Skip Elliott, *chairperson*

1. CALL TO ORDER

The meeting was called to order at 1:05 p.m.

As first order of business, Bill Erny explained that ineligible ISEA members are permitted to participate in standards development projects on an invitational basis. The standards committee must approve by a simple majority their participation. If the ineligible ISEA member participant charges a consultation fee, the fee is charged as a Group expense and distributed evenly among Group members.

Dave Goch explained committee procedures of the ISEA Product Groups. Meetings are conducted in accordance with the Robert's Rules of Order.

2. ELECTION OF COMMITTEE OFFICERS

Nominations for Committee Chairman and Vice Chairman were requested. Skip Elliott, President of Envirometrics Products Company (EPC), was nominated as Chairman

and Bob Weber of the 3M Company was nominated as Vice Chairman. The voting concluded with 6 affirm, 0 oppose, and 1 abstain for both positions.

3. REVIEW OF DRAFT 5/95 STANDARD

As a result of the last meeting in Salt Lake, a draft standard for passive air sampling devices was developed. Copies of the first draft, dated 5/95, was distributed to meeting participants for review. The purpose of the standard was stated as setting performance parameters, minimum acceptance criteria, and manufacturer reporting requirements for diffusion type sampling devices used to determine concentrations of toxic gases and vapors in working environments.

The Group set a completion deadline for a final draft for the beginning of the forth quarter of this year.

The Group began a section by section review of the draft standard. Several parked issues were identified from the last meeting. The first being the establishment of a list of potential ANSI canvassees to include in the review and balloting in accordance with ANSI procedures. It was suggested that an educational campaign be initiated subsequent to canvassing to gain wide support for this new approach in validating passive devices. It was concluded that a "peer review group" should be developed conducted initially. All Committee members were requested to submit a list of peer reviewers to ISEA before the end of July. Additionally, Committee members were requested to review the preliminary list of ANSI canvassees included in the foreword of the draft standard and develop suggested revision for Committee consideration keeping in mind umbrella organizations.

The group discussed the need for section 11, Rationale. It was stated that some explanation of why the standard was developed is needed to gain a broad range of understanding and acceptance from the industry. It was noted that this type of explanation is typically included in the foreword. Section 11.2, Goal and Objectives, was noted as duplication of sections 1.1 and 1.2, Purpose and Scope. Skip Elliott was assigned to combine section 11.2, into sections 1.1 and 1.2 for review at the next meeting. It was also requested to delete sections 11.1 and 11.2 and move Section 11.3 to the appendix.

Gus Manning was assigned to draft a statement for item 3 under section 1.3 excluding continuous reading monitors from the scope of the standard. Also a definition for sorbent will be included in section 4. The Group was requested to review all definitions and submit any suggested changes to ISEA before the next meeting.

The Level II classification was discussed. It was requested that Bill Erny check with ANSI regarding the merit of establishing an ANSI Standing Committee, chartered to evaluate and approve a manufacturer's claim for extrapolation of an analyte or a group of analytes, based on level I compliance of a similar analyte. Under this scenario, the manufacturer would be required to submit a disclosure including rationale for his request. If a third-party certification program is established for these devices, the third-party certification program would include a process to evaluate level II devices. It was suggested to include level II evaluation criteria in the appendix of the standard for guidance. Martin Harper was assigned to draft a section for Group review at the next meeting.

The Group discussed section 5, Evaluation Program and Parameters. It was suggested that a factorial evaluation option be included an it was suggested that the European protocol be used, excluding the boundary conditions. Martin Harper was requested to draft language for Group review at the next meeting.

Martin Harper was requested to draft shelf storage requirements. It was suggested that the European standard be used as a guide.

Bob Weber was requested to draft field evaluation criteria for Group review at the next meeting.

Gus Manning was requested to combine all reporting, marking and labeling requirements of section 6 and 10. It was suggested that the labeling of Type C monitors require that Type C monitors be submitted to an accredited laboratory for analysis and Type B monitors require a defined calibration protocol.

In summary it was requested that all assignments be submitted to ISEA by July 31.

4. COMMITTEE ASSIGNMENTS

Martin Harper reported on ASTM standards activity. The goal of the ASTM atmosphere monitoring committee is to develop an ISO standard and Dave Barley, chairman, has NIOSH funds to review the NIOSH protocol to use as a strawman. It was suggested that a joint effort could be pursued between ANSI and ASTM. However, the Group decided to continue with the ANSI program in a separate and parallel path to ASTM. Martin Harper was selected as the ISEA liaison ton ASTM. Martin and Skip Elliott were assigned to do a comparison between ANSI and ASTM standards.

Stefan Zloczysti was introduced to meeting participants as the chairman of the European standards committee for atmosphere monitoring devices, CEN/TC-137. Stefan explained that their committee initially considered pursuing an ISO standards but decided not to, due to the length of time to complete such a program. Stefan announced that the CEN standard is currently out for ballot and is expected to be published by the end of this year. Their next meeting is scheduled for October in Brussels. Stefan stated he would send a copy when compete to the ISEA.

Rolf Hahne Safety Director of the DOW Chemical Company gave a user's perspective on the need for effective and reliable passive samplers and expressed a need for a standard protocol to validate them. Rolf stated he would inquire at the Chemical Manufacturers Association, CMA into interest in supporting the development of a validation standard. Martin Harper will act as the point of contact an report back at our next meeting.

5. NEW BUSINESS

It was announced that SEI has issued its first passive air sampling badge certification to EPC. Bob Curtis of the OSHA Salt Lake Technical Center noted that OSHA has recognized the SEI certified badge for use by OSHA Compliance Officers through its Chemical Information File.

6. NEXT MEETING

The next meeting is scheduled for Sunday, November 5, 1995 in conjunction with the National Safety Show, Dallas Texas.

7. ADJOURNMENT

There being no further business to discuss, a motion to adjourn was accepted at 5:45 p.m.

Respectfully submitted,

William J. Erny
Technical Director

Attachment

3M 110301

Industrial Safety Equipment Association

MINUTES
Instruments Group Meeting
Thursday, May 25, 1995
Kansas City Marriott at Allis Plaza
Kansas City, MO

MEMBERS PRESENT

Air Liquide America	Margarita Porto
Biosystems Ind.	Robert Henderson
Envirometrics Products Co.	Skip Elliott
Gas Tech Inc.	Bruce Holcom
3M Company	Bob Weber
Mine Safety Appliances	Ken Acer
Neotronics	Ralph Burns

MEMBERS ABSENT

Scott Aviation	A. Perry

OTHERS PRESENT

Air Liquide America	Emerson Todd
Bacharach Inc.	Mark Coppler
RKI Instruments Inc.	Bob Pellissier
Webster, Chamberlain & Bean	Art Herold
ISEA	Bill Erny

PRESIDING — Robert Henderson, *chairman*

1. CALL TO ORDER

The meeting was called to order at 9:00 a.m.

As the first order of business, Chairman Henderson introduced three new Instruments Group members: Skip Elliott of Envirometrics, Margarita Porto of Air Liquide America, and Bob Weber of 3M. Also, two potential members were introduced: Mark Coppler of Bacharach Inc. and Bob Pellissier of RKI Instruments Inc.

2. CONSIDERATION OF MINUTES OF NOVEMBER 12, 1995

The meeting minutes of November 17, 1995 were approved as presented.

ANSI/ISEA 102-1990

Bill Erny reported that ANSI/ISEA 102-1990, "American National Standard for Gas Detector Tube Units," is due for review in accordance with the 5-year review policy of the American National Standards Institute. Ken Acer was assigned to lead the revision effort. Bill Erny was assigned to request an extension of ANSI.

4. DRAFT ISA/NEC UPDATE

Mark Coppler, Chairman of ISA 1213, reported on the ISA Combustible Gas Committee. The Combustible Gas Standard, ANSI/ISA 1213 was reviewed in February and has been submitted to the program committee for review and approval as an American National Standard.

The ISA "Recommended Practice" is up for review in 2 years. The committee has begun their initial review. An important new issue is the impact of new technologies.

It was reported that the ISA standards for toxic gases (CO, NH3, C1, Ox), are out for ballot approval. Comments will be considered at ISA's next meeting in June in Tucson, AZ. Bruce Holcom volunteered to act as ISA liaison to the Instruments Group. Bruce was requested to submit copies of the toxic gas standards to ISEA for circulation to members of the Instruments Group. It is expected they will be approved as final by the end of 1995.

Chlorine was identified as a potential controversy due to a proposed protocol to produce concentrations of Chlorine to tight tolerances.

5. NFPA 306

Ken Acer reported that NFPA 306 is due for review by the end of Fall. Two important issues are the oxygen deficient requirement of 22% which conflicts with the 23.5% OSHA Confined Space requirement and calibration before and after use issue. It was suggested that the Group make a clear recommendation to the NFPA 306 Committee to establish consistent criteria. Bill Erny was requested to send out copies of 306 to Group members for review and comment.

6. OTHER STANDARDS ACTIVITIES

Mark Coppler reported that a draft ISA standard has been developed on generic performance criteria for toxic gas monitors. ISA 9207 would include requirements for monitors covered by ISA standards 9201 through 9206. The project was motivated by CEN TC116/137 which has developed a similar document.

7. CEN STANDARDS

It was discussed whether a published comparison exists between CEN and U.S. standards and whether the Instruments Group should take on such a project if none exists. Mark Coppler noted that a project has been undertaken by the ISA. Bruce Holcom volunteered to report back to the Group on future ISA project activity. No Group action was determined at this time.

8. PASSIVE MONITORS SUBCOMMITTEE REPORT

Bill Erny and Skip Elliott reported on recent activity of the passive monitors subcommittees (PMS). The PMS had their second meeting on Sunday afternoon. The objective of the PMS is to develop standard validation procedures for passive diffusive sampling devices and publish as an American National Standard. Skip Elliott has been elected as chairman and Bob Weber as Vice Chairman. The next meeting of the passive monitors subcommittee is tentatively scheduled in conjunction with the National Safety Show in Dallas which runs from November 6-8. A specific meeting date will be announced later.

9. CONFINED SPACE STANDARD, ANSI Z117

Bill Erny and Bob Henderson reported the results of balloting Z117. It was explained that ISEA's comment regarding the definition of "entry" into a confined space was rejected. As a result, ISEA voted against the standard as written. ISEA requested that an entry be defined when "any part of the body" of an entrant breaks the plane of a confined space in accordance with OSHA regulations. The approved language defines an entry when any part of an entrant's face breaks the plane. Attached to these minutes is the Z117 Committee rationale for rejecting the ISEA suggestion which in part uses the 1994 NIOSH publication "Worker Deaths in Confined Spaces" as support documentation.

The Group determined that no further official appeal action would be initiated at this time. However, Bill Erny was requested to contact ANSI to ensure our comments were received and recorded.

10. OSHA PROPOSED RESPIRATORY RULE, 29 CFR 1910.134

Bob Henderson reported that comments were submitted on behalf of both the ISEA Respiratory Protection and Instruments Groups. Specifically the Instruments Group raised concern over the fact that OSHA has removed a requirement for continuous CO monitoring on oil lubricated compressors. ISEA comments recommended the ANSI Z88.2-1990 requirements (see attached) that requires periodic sampling as directed by the program administrator. It was noted that ISEA has historically supported OSHA's adoption of Z88.2 in their regulations.

Bill Erny reported that the OSHA public hearings are scheduled from June 6-20. ISEA is scheduled to present testimony on June 14.

11. AIHA GAS AND VAPOR DETECTION COMMITTEE

It was reported that NIOSH is currently drafting standards on CO, H2S and Tritector monitor performance. Mary Woebkinberg of NIOSH-Cincinnati is the project group leader. Bruce Holcom was assigned to contact NIOSH and collect specific information for Group distribution.

A passive monitors round table is scheduled for Friday and is being chaired by Martin Harper of SKC Instruments. Ken Acer is attending and was requested to report the results of their discussion to the Group before the next meeting.

A round table on "Emergent Technologies," chaired by Steve Day is scheduled for the Fall.

Bob Henderson was requested to pass on the minutes as soon as they are available.

12. AIHA CONFINED SPACE COMMITTEE

Bob Henderson reported on the meeting that transpired on Monday, May 21. The main topic of discussion focused on performance characteristic and calibration requirements of sensors used in confined space applications. Bob was requested to pass along the official meeting minutes as they become available.

It was suggested that the Instruments Group should put together a position paper on calibration frequency of instruments used in confined space applications. It was noted that the need for such information is paramount to end users. A cutoff date of June 15 was established for submittal of Group comments to ISEA. All comments will be circulated to Group members and a position paper will be developed.

13. NEW BUSINESS

An overview of outside representation identified the following:

Bruce Holcom	-	ISA, NIOSH
Ken Acer	-	NFPA 306
Bob Henderson	-	AIHA Gas & Vapor Committee
Bob Weber	-	AIHA Respiratory Committee

14. NEXT MEETING

The next meeting of the Instruments Group is scheduled in conjunction with the ISEA Mid-Year Meeting which is held from November 13-15 at the Ritz-Carlton Pentagon City, Arlington, Virginia. The specific meeting time, room location and agenda will be presented at a later date.

15. ADJOURNMENT

There being no more business to discuss, the meeting was adjourned at 10:25 a.m.

Respectfully submitted,

William J. Erny
Technical Director

Attachment

Table 4 – Periodic air sampling guidance for compression

Type/sample	Oil lubricated	Non-oil lubricated	Combustion engine powered
Water vapor	X	X	X
CO	X		X
Condensed hydrocarbon	X		X
CO_2			X
Odor	X	X	X

NOTES

1 When using air compressors, intake location shall be carefully selected and monitored closely to ensure air supplied to the compressor is of adequate quality.

2 No frequency for periodic checks of air quality is specified, due to wide variation in equipment type, use and working environments, and operating experience.

3 Continuous monitoring of temperature and carbon monoxide are not required.

4 For non-oil lubricated compressors that operate at less than 35 psi, no sampling for water is required.

5 These requirements apply to systems designed for breathing air, other air-supply systems need to be evaluated on a case-by-case basis for the type and frequency of testing.

10.5.4.2 A compressor shall be constructed so as to avoid entry of contaminated air. For all air compressors, including portable types, the air intake location shall be carefully selected, and monitored closely to ensure continued quality of air supply to the compressor. The system shall be equipped as necessary with a suitable in-line air-purifying sorbent bed and filter to further assure breathing air quality. Maintenance and replacement/refurbishment of compressor and associated air-purifying/filter media shall be performed periodically, by trained personnel following manufacturer's recommendations and instructions.

10.5.4.3 As part of acceptance testing, and prior to initial use, representative sampling of the compressor air output shall be performed to ensure that it complies with the requirements in 10.5.1 and 10.5.4. To ensure a continued high-quality air supply, and to account for any distribution system contaminant input, a representative sample should be taken at distribution supply points. Samples should be collected on a periodic basis, as directed by the program administrator. Specific test recommendations are given in table 4.

10.5.4.4 The dew point of breathing air used with supplied air respirators should be lower than the lowest ambient temperature to which any regulator or control valve on the respirator or air-supplied system will be exposed.

10.5.4.5 Breathing air couplings shall be incompatible with outlets for nonrespirable plant air or other gas systems to prevent inadvertent servicing of supplied-air respirators with nonrespirable gases. Breathing air outlets shall be labeled.

10.5.4.6 Breathing gas containers shall be marked in accordance with ANSI/CGA C-4-1990. Further details on sources of compressed air and its safe use will be found in CGA G-7-1988.

Industrial Safety Equipment Association

Meeting Report
Passive Dosimeter Manufacturers
Tuesday, October 25, 1994
San Diego, CA

ATTENDING

Skip Elliott	Envirometrics Products Co.
Lloyd Kent	Matheson Gas Products
Rena Kirkpatrick	Assay Technology
K. Kirolos	Gilian Environmental Corp.
Mike Marselli	Sensidyne
Bob Curtis	OSHA
Ed Zimowski	OSHA
Dan Shipp	ISEA
Bill Erny	ISEA

1. PURPOSE

This meeting was called to discuss the possible development of an ANSI standard for passive monitors for detection an measurement of hazardous contaminants. Mr. Elliott noted the product was developed to meet a need for a means of measuring and immediately determining the level of toxics. He noted that market enthusiasm is tempered by the need for some assurance of product performance. Third party validation of manufacturers claims will provide that assurance, he said, but such certification requires a uniform test protocol.

A test protocol is in existence, developed by a NIOSH researcher. OSHA uses part of that protocol now. But there is a general preference for a voluntary standard, so manufacturers can have a role in its development and will be more likely to support it.

ISEA staff described the association's structure and procedures for developing American National Standards.

2. DISCUSSION

Among the issues raised in discussion were the following:

a. This standard would formalize a method for evaluating a new technology.

b. Third-party testing can be used to validate a manufacturer's claims for a product, or to verify that a product meets a minimum level of performance.

c. What should be the scope of the standard? Should it only cover direct-reading passive monitors or should it include sorbent monitors that have to be sent to a lab for processing? Should it include digital display monitors?

d. OSHA wants to be able to use passive monitors, but needs assurance that they will work.

e. ISEA staff explained that a standard could be a new ANSI standard, a new ANSI/ISEA standard, or a revision to the existing ISEA/ANSI gas detector tube standard.

f. An interim protocol -- ISEA or OSHA - could be used while the ANSI standard is being developed and reviewed.

3. DECISIONS AND NEXT STEPS

The group will have to determine the scope of a proposed standard. They agreed to hold another meeting to develop these criteria. In preparation for this meeting, the participants will send the ISEA the names of other manufacturers. The ISEA will invite companies making on-site reading passive monitors, long-term detector tubes and sorbent monitors. They will not include electrochemical monitors at this point.

Mr. Curtis offered the OSHA Technical Center in Salt Lake City as a site for this initial meeting, as well as a subsequent technical meeting. He and Mr. Erny will work out the details of the meeting. Mr. Elliott will draft the letter of invitation, to be mailed by ISEA to prospective participants.

Recorded by Daniel K. Shipp

cc: The Instruments Group

ISEA Industrial Safety Equipment Association

MINUTES
Passive Monitor Standards Committee
of the
Instruments Group
Sunday, November 5, 1995
Stouffer Dallas Hotel
Dallas, Texas

MEMBERS PRESENT

3M Company	James Kvickstad
Envirometrics Products Co.	Skip Elliott
Mine Safety Appliances	Katie Spear
SKC Inc	Martin Harper

OTHERS PRESENT

Assay Technology	Gus Manning
Webster, Chamberlain & Bean	David Goch
ISEA	Bill Erny

PRESIDING — Skip Elliott, *chairperson*

1. CALL TO ORDER

The meeting was called to order at 10:00 a.m.

As the first order of business Chairman Elliott outlined the following three goals of the Committee meeting today:

- Review and approve the draft standard for release to the informal peer review group;
- Approve the informal peer review group members;
- Consider and vote on the alternative section 6 on evaluation parameters submitted by Martin Harper.

Martin Harper reported on ASTM Committee activity. Martin explained that Dave Bartley is the NIOSH representative to the ASTM D44 Committee on Air Sampling. Allen Ishe of Miles is the chairman of the D44 Committee. Richard Danchik of ALCOA is the chairman of the D44.02 subcommittee on workplace atmospheres. Martin has been maintaining communications with Dave Bartley who was assigned by the D44.02 Committee to update the NIOSH protocol.

However, Dave has agreed to postpone revision of the NIOSH protocol until he has had a chance to look at the ISEA draft and will consider adopting the ISEA requirements as the NIOSH criteria. It was further explained that ASTM may adopt the ISEA/ANSI standard as an ASTM/ANSI standard.

2. CONSIDERATION OF MINUTES

The minutes of May 21 were approved as presented.

3. REVIEW OF DRAFT 10/11/95 STANDARD

The Group agreed to modify the title of the standard to more accurately describe the type of products included. The word TYPE was replaced with SAMPLERS AND MONITORS.

The Group revised section 1, Purpose and Scope. Section 1.1 was replaced with the following: "This standard enables manufacturers and users of diffusive samplers and monitors to adopt a consistent approach to product evaluation." The revised language was developed to better explain the purpose of the standard. It was noted that the previously included background information was inappropriate and should be deleted.

Section 1.3 was revised to delete a Type C device. It was decided to combine the Type A and Type B devices into Type A - On-site Reading Devices. The previous Type C devices were reclassified as Type B - Laboratory Analyzed Devices. It was noted that the separation of Type A and Type B was redundant and not needed to include all types of passive monitoring devices.

Section 2 was modified to eliminate Level I and Level II compliance classifications. It was agreed that the reporting requirements required by the standard are sufficient to ensure that proper extrapolation criteria are followed since they require a manufacturer to disclose and provide rationale for exclusion of any test method due to extrapolation. The following was developed and included under section 2.1:

"Compliance with this standard shall be established by a test report which details adherence to the test methods and evaluation parameters outlined in this standard.

If it is known that a certain sampler or monitor is unaffected by a specific environmental influence, the relevant tests may be modified to examine only the factors likely to have an influence. The rationale for any modification to the test methods and evaluation parameters must be fully outlined in the test report."

An alternate proposal for section 6 was presented by Martin Harper for consideration by the committee. Martin explained that the alternate section 6 was developed to promote international harmonization. Martin Harper explained that

complete harmonization is unfortunately not possible at the present time since the European Standards specify accuracy limits and evaluation criteria. However, alternate section 6 was written so that products evaluated under the ANSI criteria could be included under the European and NIOSH criteria. After review and modification, the alternate section 6 was approved for adoption to replace the current section 6 with the following exceptions: the current section 6.1.6, Quality Control; section 6.1.9, Inter-reader variability; and section 6.1.10, Readout time were retained.

Section 7 was removed since it is already included in the newly adopted section 6.

Section 8 was re-titled "Quality Control Requirements" and renumbered as section 7. Section 8.2, "Reporting and Labeling Requirements" was made its own section 8.

Martin Harper volunteered to review the reporting and labeling requirements section to ensure it coincides with the newly adopted section 6.

The Group reviewed and made minor revisions to the definitions section to clarify and remove extraneous definitions that are not needed or used within the body of the text.

The Group reviewed a proposed section on Field Test that was developed by Bob Weber of 3M. It was proposed that Bob's proposal replace the appendix. However, after review the Group concluded that the current language was close to achieving the objective of describing generally the importance of field testing. It was noted that this standard should not and does not address field testing criteria. Gus Manning volunteered to review the appendix language on field evaluation and coordinate his revision with Bob Weber. Martin Harper suggested that Gus use the CEN section on field evaluation as reference.

Skip Elliott was assigned to incorporate all approved changes into the draft standard within the next two weeks. Bill Erny was assigned to distribute the revised draft to Group members for review. ISEA will set up a conference call of the Passive Monitors Group for December 20 at 11:00 a.m. EST. The objective of the call is to discuss and resolve all concerns with the draft and to confirm approval of the draft for submission by the end of 1995 to the informal peer review group. The informal peer reviewers will be requested to return comment to the ISEA by the end of March. The Passive Monitors Group will meet at the AIHCE in Washington to review the comments and approve a final draft for submission to ANSI as an American National Standard.

Martin Harper announced that a round table discussion is scheduled for the AIHCE, "Accuracy Considerations for Air Sampling and Analysis Methods".

Attached is the round table abstract. Martin explained that a major topic of discussion will be the ISEA draft diffusive sampler standard. It was agreed that the Group should include the feedback generated at the round table with the comments received by the peer reviewers.

In conclusion it was agreed that a final draft standard is expected for completion for submittal to the ANSI canvass list by the spring of 1996 and that a final published document could be available by the fall of 1996.

4. CONSIDERATION OF THE INFORMAL PEER REVIEW GROUP

The Group approved the following list of 10 peer reviewers that will be asked to review and comment on the ISEA draft:

- Dr. Gene Feigly, University of South Carolina
- Richard Brown, Health & Safety Laboratory
- Lee Montieth, University of Washington
- Mark Puskar, Abbott Laboratories
- Dave Bartley, NIOSH
- Dr. Stephan Zloczysti, CEN
- Rick Cee, OSHA
- Paul Michael,
- Rolf Hahne, Dow Chemical Company

5. NEXT MEETING

The next meeting was tentatively scheduled for the third week in May in conjunction with the American Industrial Hygiene Conference which is being held in Washington D.C.. More specific information will be determined at a later date.

6. ADJOURNMENT

There being no further business to discuss, a motion to adjourn was accepted at 4:25 p.m.

Respectfully submitted,

William J. Erny

William J. Erny
Technical Director

Attachment

List of passive monitor peer review group
11-9-95

Dr. Gene Feigly
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Dept. of Environmental Health Sciences
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Phone: (803) 777-7739
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Mark Puskar, PhD
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Dave Bartley
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Paul Michael
Lab Director
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Rolf Hahne
Dow Chemical Company
1803 Building
Midland, MI 48674
Phone: (517) 636-9065

ISEA **Industrial Safety Equipment Association**

MINUTES
Instruments Group Meeting
Tuesday, November 14, 1995
Ritz-Carlton Pentagon City Hotel
Arlington, VA

MEMBERS PRESENT

Margarita Porto	Air Liquide America
George Baker	Air Liquide America
Robert Henderson	Biosystems Inc.
Skip Elliott	Envirometrics Products Company
Ken Acer	Mine Safety Appliances Co.
Jim Kvikstad (for Bob Weber)	3M Company
Ralph Burns	Neotronics of North America

MEMBERS ABSENT

Bruce Holcom	Gas Tech Inc.
Al Perry	Scott Aviation

OTHERS PRESENT

Pat Gleason	Safety Equipment Institute
Bruce Clash	ISEA

PRESIDING — Robert Henderson, Chairman

1. CALL TO ORDER
The meeting was called to order at 9:00 a.m.

2. CONSIDERATION OF THE MINUTES
The meeting minutes from May 25, 1995, meeting were approved as presented.

3. GAS DETECTION TUBE UNITS – ANSI/ISEA 102-1990
The ISEA would like to obtain an extension from ANSI for the standard to remain in effect beyond its five year lifetime. Bill Erny at ISEA was given the task of following up with ANSI on this issue.

4. REPORT ON PASSIVE MONITOR STANDARDS COMMITTEE
Chairman Skip Elliott reported on the work being done by this committee, which held its first meeting in May at the American Industrial Hygiene Show in Kansas City. Skip explained that the objective of this standard is not to set performance criteria, but rather to set testing conditions and marking requirements for passive monitors. Martin Harper of SKC Inc. has looked into what Europe is doing. Skip noted that OSHA has been

involved in this project since its inception and is keenly interested to see such a standard developed for passive monitors since it would provide more feasible alternatives in characterizing workplace exposures. Skip also stated that a joint ASTM/ANSI standard is being discussed.

Skip reported that at the Dallas meeting, the committee approved a draft standard for circulation to an "advisory panel" including government officials, academia and industry professionals. The draft will be sent to the panel in January for their input and comment. The committee will meet next May at the AIHCE in Washington, D.C. and expects to begin ANSI canvassing shortly thereafter.

5. ISEA INSTRUMENT SPECIFICATION WRITING ACTIVITIES

It was reported that in 1992, Underwriters Laboratories (UL) published a standard, UL 2034, for carbon monoxide (CO) detectors. The Consumer Product Safety Commission will conduct a public hearing on January 23-24, 1996, to receive scientific, medical and other technical information about CO detectors and the voluntary standard for them. The subject of whether the ISEA should get involved in performance criteria for these detectors was discussed. It was felt that ISEA should have some input, but a plan for how to do so was not discussed. Ken Acer will be coordinating the ISEA action plan.

6. CONSENSUS ISEA CALIBRATION STATEMENT

There was a discussion on what elements the ISEA calibration statement should contain: 1) Instruments should be maintained in accordance with manufacturers' specifications; 2) Instruments should be checked for accuracy before any day's use; and 3) Any detector with readings any amount lower or 10 percent higher should be adjusted before use.

Two other suggestions were made: 1) If a portable instrument is assigned to one user who finds that it needs calibration less often, then calibration can be done based on the performance history of that instrument as it is known by that user; and 2) Calibration can be done less frequently on instruments that will be used exclusively in areas known to have a low probability of being hazardous.

Discussion ensued on what to do with the statement once it is finalized. It was suggested that it be reviewed by the ISEA Quality Assurance Committee so that it would then become an official ISEA document. The idea that it then be incorporated into an editorial article in various publications was also discussed. Bob Henderson will circulate a statement to the Group members when it is drafted.

7. REVIEW OF NFPA 306 ACTIVITIES

Ken Acer informed the Group that this standard is in the five year review process. The major issue for instruments manufacturers in this work practices in shipyards standard is oxygen high alarm set points. The first NFPA 306 meeting is in Arlington, VA, on December 12. Ken will continue to follow developments on this issue and will keep the Group informed.

8. DRAFT ISA/NEC UPDATES

Bob said that he will have ISEA staff distribute the memo on this subject from Bruce Holcom. It was asked of Pat Gleason if SEI has an interest in certifying these

products. Pat said she would check with Clayton labs and let Bob Henderson know the response.

9. ANSI Z-117 (CONFINED SPACES) UPDATE

It was said that Barry Phillips of Racal Health and Safety is the official ISEA representative to this committee. He is working to determine where this issues stands at the moment.

10. OSHA 1910.134 (RESPIRATORY PROTECTION) UPDATE

This issue has some tangential interest for the Instruments Group. It is possible that the draft will be withdrawn and probably reissued as a proposed rule. ISEA is trying to get NIOSH and OSHA to coordinate their approach on respiratory protection.

11. REVIEW OF AIHA GAS AND VAPOR CONFINED SPACED COMMITTEE ACTIVITIES

The Gas and Vapor Confined Space Committee round table for the 1996 AIHA conference will be centered on sensor performance and calibration issues. Bob Henderson will keep the Group informed of the Committee's activities.

12. SELECTION OF REPRESENTATIVES TO STANDARDS COMMITTEES

Representatives to the various committees were selected:

NFPA 306	Ken Acer
AIHA Gas and Vapor	Bob Henderson
AIHA Confined Space	Bob Henderson
ISA Instruments	Bruce Holcom

13. FUTURE ANSI/ISEA STANDARDS WRITING ACTIVITIES

No items were discussed.

14. NEW OR UNFINISHED BUSINESS

It was mentioned that OSHA will be looking at 1910.1000 permissible exposure limits soon. Skip Elliott volunteered to learn the status of OSHA's review and will talk to Bill Erny at ISEA to find out what The Jefferson Group is doing in this area.

It was asked if instruments are included in the comparison of international standards project that is underway by ISEA's International Trade Committee. Bob Henderson will talk with committee chairman Roger Gehrig about the project.

Industrial Scientific Corporation was mentioned as a company that should be a member of the Instruments Group. Dave Wagner is the company's new product manager. ISEA staff will follow up with this prospect. AIM has verbally indicated that it will join the ISEA in the spring.

Questions concerning the status of the Eye and Face Group's statistical survey were raised. There was a consensus that the Instruments Group would like a report on this project at the next meeting in order to see whether a similar survey would be feasible for instrument manufacturers.

15. NEXT MEETING DATE

The next meeting will occur during the AIHA show in Washington, D.C., during May 18-24. The exact date will be determined once the show meeting calendar is reviewed.

Respectfully submitted,

Bruce R. Clash

Bruce R. Clash
Public Affairs Director

3M 110317

OSHA Salt Lake City — Date [redacted] 94

PASSIVE MONITOR

attendees:

ISEA: Bill Erny — OSHA: Bob Curtis; Rick Cox; Warren Hendricks

Gus Manning: Assay
Marshall Parker: Clayton — Alan Hart: Protech
Kathi Spear: MSA — Larry Locker:
Ralph Burns: Neutronics
Martin Harper: SKC
Victor Elia: National Carmel Assoc etc.
Skip Elliott: Enviromedics
Ron Robertson: Sensidyne

ANSI: Given Verbal Go!
SET - send in project request.

next mtg — Closed mtg of ISEA members
- look @ structure of committee
- Invite issues
- solicit other member list.

estimated time of program - 2 years.

→ possibility of have a combination ANSI/ASTM Standard - then submit to ISO. - this would create a international/world std.
ANSI - VS ASTM/ANSI ⇒ ISO

→ Bob Lewis - EPA contact — EPA is now writing — NIOSH (R) DAVE Bartley - ASTM MARTIN able Gene Kennedy

→ ASTM is writing a Standard on Passive Monitor
"Prudent Contact" — D2206 - ASTM - [redacted] - Pittsburg Mtrs — Rick Deanchik — schedule ?

OSHA is interested because:
- Bob Curtis - Policy on 3rd party certification — not doing it at all - National CIH
- CONVINCE employers to do more monitoring
- Ideal OSHA inspector - look @ exposure - to spot checking
- look @ setup → need to characterize exposure. → give evaluation for not sampling

excited: Practice CIH - still let evaluate the protocol thing

Tomorrow "class" - Std will give ~~out~~ SAH config Data to use a DMT

- Box ? - more time

⇒ Objectives: Develop a Test protocol Std for Device mnfrs

- outline testing requirements for validation

Bob Curtis: ⇒ Changing IH testing and the world

⇒ Concept of painting the "Box" ~~limiting~~ concept ?

⇒ Pass a Generic device and/or verify classic made mfg

- Define standard testing conditions
- test methods

⇒ Test Claims of mfg
⇒ should encourage ~~[illegible]~~ technology
⇒ should encourage ~~[illegible]~~ by suppliers
⇒ uniform terminology
⇒ sets operating parameters of device = Box concept"

overall goals

Scope + Standard
(what devices are covered)

validation

SKC (Merlin concerned about doing work over again.)

Diffusion Sampler

~~[illegible]~~ collects Contaminants ~~[illegible]~~ down the ~~[illegible]~~ ~~[illegible]~~ is based on Diffusion

Middle Step ~~[illegible]~~ some ~~[illegible]~~ absorbent media may required additional testing such as electrochemical sensors

Device where testing is based on diffusion. ~~[illegible]~~ ~~[illegible]~~ Note: Some added Sorbent media may require additional performance criteria, such as electrochemical sensors.

3M 11281

Date

SKC leveraging decision

- leverage the NIOSH
- they do not want to pay more $ for validation
- alot of $ spent on NIOSH procedures?

SUMMARY.

~~Thing~~

~~Hand~~ Develpm - Grant comm

OSHA's ~~mod~~ comm

M

Pg 2

Date

Scope

Possible Elements of

- No Active pump - Diffusive
- look @ Occupational Ex limit, TLV etc...
- similar label requirements / Product Inserts
- QA programs / ER passes VS Time Exposure chart.
- Need to help user.
- Criteria to select
- Martin presented a NEW SRC approach

- agreed that NIOSH + CEN criteria should be evaluated.

+ - Fractional
- Passive VS
- sampling size

TSO Std for generating Stds — look @ CEN

ORDER ASTM Document D4597-87 std Practice Atmospheric to collect organic gases + vapors w/ activated charcoal Diffusional Samplers.

What is the status of Exposure Assessment Std.?

* May deviate from the ±25 accuracy requirement may decide to let mfg set the accuracy
- AIHA accreditation will be required for!
- GRAU / Reserve issue?
- Need to stay w/ committee — may impact sensor program.

Date
5-24-94

- ISEA/ANSI Committee meeting
-
- Election of officers:
  - Skip Elliott – Chair
  - Weber – Vice Chair.

Martin Harper DAVE Bartley (ASTM) NIOSH

- might develop a joint protocol w/ ASTM / ANSI
- Workplace atmospheres etc (title)?
  Committee
  → project for the group is to look diffusion monitors
  - check w/ Swidy

Talk w Toni – European stds
– 838 – next for vote

- Chemical Mf Asso
  - Harper trying to push (Rolf? – DOW) for mfgs to mandate the monitors be validated.

- Application issue is up to user

- At the next draft we will circulate to friendly peer review.
  - send list of people to Bell Army who to review

Note – More & More testing

Date

Sept 30 736-2593
1-800-243-4630

726-3999

Oct 17

password
mailbox

ISEA Industrial Safety Equipment Association

October 20, 1995

TO THE PASSIVE MONITORS
STANDARDS COMMITTEE:

Draft standard and friendly peer review

Attached is a revised agenda for November 5, the draft standard version 10.11.95 which incorporates all change as a result of our last meeting. Also a suggested alternative section 6, "Evaluation Parameters", has been submitted by Martin Harper and is attached separately for your review. Lastly, a list of friendly peer reviewers is included which needs to be approved at the November 5 meeting in Dallas. The main purpose of the Dallas meeting is to approve both a peer review group and a draft standard that we can submit to the peer review group to obtain important feedback from a user's perspective.

Please review the enclosed materials closely and be prepared to discuss them at the meeting in Dallas. If you are unable to attend the Dallas meeting, you my submit comments to me via FAX at (703)528-2148 or contact me directly at (703)525-1695. I look forward to seeing you all in a couple weeks and having a very productive session.

Sincerely,

William J. Erny
Technical Director

3M 110326

1901 N. Moore Street, Suite 808, Arlington, VA 22209 • Tel. (703) 525-1695 • Fax (703) 528-2148

Meeting of the
PASSIVE MONITORS STANDARDS DEVELOPMENT COMMITTEE

November 5, 1995
9:00 a.m. to 5:00 p.m.

Stouffer Dallas Hotel
2222 N. Stemmons Frwy
Dallas, TX

Revised - A G E N D A

1. Call to Order at 9:00 a.m.

2. Consideration of May 21, 1995 meeting minutes

3. Committee Assignments:

   - Group Input - Friendly Peer Review and ANSI Canvassees
     - Approve a peer review list
     - Review of all Definitions

   - Skip Elliott - Rationale and History of Standard
     - Comparison Between ANSI and ASTM Standards
     - Update Draft Standard

   - Gus Manning - Continuous Reading Monitors
     - Definition for Sorbent
     - Combine Reporting, Marking, and Labeling Requirements

   - Bill Erny - ANSI Standing Committee for Level II Evaluation

   - Martin Harper - Level II Evaluation Criteria (Appendix)
     - Factorial Evaluation Criteria
     - Rate/Capacity Criteria
     - Shelf Life Requirements
     - Comparison between ANSI an ASTM Standards
     - Report of CMA Support for ANSI Standards Development

   - Bob Weber - Field Evaluation Criteria

4. Review and approval of a draft for release to the review group

5. New Business

6. Next Meeting

7. Adjournment

List of passive monitor peer review group
10-20-95

Dr. Gene Feigly
University of South Carolina
School of Public Health, Dept. of Env. Health Sciences
Room 311
Columbia, SC 29208
(803)777-7739
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Ron Roberson
Sensidyne, INC.
16333 Bay Vista Drive
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(800)457-3444
F: (813)539-0550

Kim Chapman
Eilian Environmental
2421 Bowland Parkway, unit 102
Virginia Beach, VA 23454
(804) 431-2260
F:(804)431-2255

Richard H. Brown
Health & Safety Laboratory, U.K.

Lee Monteith, ACGIH
University of Washington

Mark Puskar, PhD
Manager, Corp Industrial Hygiene Lab
Abbott Laboratories
1401 Sheridan Rd, Dept 038A
Chicago, IL 60064
(708)937-4520

INDUSTRIAL SAFETY EQUIPMENT ASSOCIATION

[redacted]

PLEASE DELIVER TO THE PERSON DESIGNATED FOR YOUR COMPANY. THANK YOU!

Company	Representative	Fax #
Air Liquide America Corporation	Margarita Porto	410-228-4251
Biosystems Inc.	Robert Henderson	203-344-1068
Enviromentrics Products	Walter H. Elliott	803-740-1721
Gas Tech Inc.	Bruce Holcom	510-794-6210
3M Company	Robert A. Weber	612-736-7344
Mine Safety Appliances	Kenneth Acer	412-776-3280
Mine Safety Appliances	Wayde B. Miller	412-967-3058
Neotronics N.A.	Ralph Burns	404-967-1854
SKC, Inc.	Martin Harper	414-941-2184
Scott Aviation	Al Perry	716-683-5530
Webster, Chamberlain & Bean	David Goch	202-835-0243

To: ISEA Instruments Group

From: Cristine Z. Fargo

Date: November 6, 1995

Re: Instruments Group Meeting, November 14, 1995

Attached please find a revised agenda for the upcoming Instruments Group meeting on Tuesday, November 14, 1995 at the Ritz-Carlton Pentagon City from 2:15 PM to 5:00 PM. If you have any questions, please feel free to contact me at 703-525-1695.

Cristine Fargo

FAXED 11-6-95 Total 3 pages

9/19/95

3M 110329

INDUSTRIAL SAFETY EQUIPMENT ASSOCIATION
1901 North Moore Street, Suite 808
Arlington, Virginia 22209

Instruments Group Meeting

Ritz-Carlton (Pentagon City) Hotel
Arlington, Virginia

Tuesday, November 14, 1995
2:15 p.m. to 5:00 p.m.

AGENDA (revised 11/6/95)

1. Meeting Called to Order by Chairman Henderson
2. Roll Call and Introductions
3. Approval of Minutes of May 25, 1995 Meeting
4. Gas Detection Tube Units - ANSI/ISEA 102-1990
   - ANSI 5 year review - Reaffirm or Revise?
5. Report on Passive Monitor Standards Committee - *Skip Elliott*
6. ISEA Instrument Specification Writing Activities
7. Consensus ISEA Calibration Statement - *Bob Henderson*
8. Review of NFPA 306 Activities - *Ken Acer*
9. Draft ISA/NEC Updates - *Bruce Holcom*
10. ANSI Z-117 (confined spaces) Update
11. OSHA 1910.134 (respiratory protection) Update
12. Review of AIHA Gas and Vapor and Confined Space Committee Activities - *Bob Henderson*

13. Selection of Representatives to Standards Committees
    - NFPA 306
    - AIHA Gas and Vapor
    - AIHA Confined Space
    - ISA Instruments

14. Future ANSI/ISEA Standards Writing Activities

15. New or Unfinished Business

16. Next Meeting Date

3M Company
3M OH & ES Division
3M Center Bldg 260-3B-09
St Paul , MN 55144-1000

Fax Cover Sheet

DATE JULY 11, 1995

TO:	Bill Erny	**PHONE:**	703-525-1695
	ISEA	**FAX:**	703-528-2148
FROM:	Bob Weber	**PHONE:**	612-737-4459
	3M Company	**FAX:**	612-736-7344

RE: Appendix on Field Testing

Number of pages including cover sheet: [3]

Message

Hi Bill;

Enclosed you will find the draft appendix on field testing that should be included in the diffusion monitor validation protocol. I have some more to add, but because of time constraints I haven't been able to complete, however I thought I should send what I have. I plan on completing sometime in August. I will forward the rest when later.

Talk to you later.

Bob Weber, CIH

Senior Technical Service Representative

Appendix ?

Field Test

Introduction

Laboratory validation of diffusion monitors defines the operating parameters of the device and accounts for many of the variables that may be encountered in the field; however, there may be factors in the workplace that will influence the performance of the diffusion monitor that cannot be anticipated in laboratory validation studies. For example such factors as intermittent and rapidly changing concentrations, or the presence of interference's. Therefore testing the diffusion monitor under actual field condtions is recommended.

Several factors need consideration before conducting field evaluations. First, the true concentration is not known and therefore must be estimated with an independent method. However, the independent method is subject to errors just as the diffusion monitor. Therefore the difference between the two should not be interpreted as a bias. Second, the use of side-by-side sample collection must be carefully monitored. Sampling devices, either active or diffusive, placed on an individual's right and left lapels may give different results; although each may give an accurate measurement of the concentration to which they were exposed. The differences in side-by-side sampling can be attributed to the existence of concentration gradients in the sampling area. Concentration gradients may be due to the individual's location to the contaminant producing equipment or process, direction in which the individual is facing during exposure, and the type of work being performed. Third, the environmental factors in the field must be determined to insure that the diffusion monitor and independent method are being conducted within their operational ranges.

Field Test Methods

Evaluation of diffusion monitors in the field can be conducted by two different sampling techniques. The first technique, personal sampling, involves having individuals wear both the diffusion monitor and independent sampling device simultaneously. This technique is subject to errors outlined earlier. The second technique, field chamber sampling, involves exposing both sampling techniques to an atmosphere of homogenous analyte concentration and a face velocity sufficiently high enough to prevent diffusion monitor starvation. Workplace air is drawn into a chamber where a statisically significant number of sampling devices will simultaneously collect the contaminants. Field chamber sampling may not represent a typical worker exposure, however it does eliminate errors that are associated with personal side-by-side sampling.

Field Chamber Sampling

Include technique, sample size, statistics and diagram of chamber.

Personal Sampling

Include technique, sample size, and statistics.

Annex C (informative)

Field tests - Paired comparisons

C.1 Introduction

Although the diffusive uptake will have been determined, and any effect of environmental factors checked, in the laboratory tests, there may be some factors existing in the workplace that will influence the performance of a diffusive sampler. Such factors may be rapidly changing concentrations, or the presence of unanticipated interferences, or the presence of the analyte either as suspended matter or sorbed onto suspended matter. Tests should therefore be conducted under conditions typical for the intended use of the diffusive sampler, to determine the presence of any systematic difference between the sampler results and those of an independent method.

NOTE:
In this context neither the diffusive sampler nor the independent method gives the "true" result, as both are subject to error. The difference between individual paired results should not therefore be interpreted as a bias.

C.2 Requirement

C.2.1 Paired sample t-test

The mean value of [log x - log y] should not be significantly different from zero. If it is, it represents a systematic difference between the measurements made by the diffusive and independent methods for which an explanation should be sought.

C.2.2 Regression analysis

The 95 % confidence limits of the values a and b (see C.4.2.2) should respectively embrace zero and unity. If not, a deviation represents a systematic difference between the measurements made by the diffusive and independent methods for which an explanation should be sought.

NOTE:
Most computer programs for linear regression analysis assume x is without error and slightly underestimate b as a result. The correlation coefficient, r, has only qualitative value in this context.

C.3 Materials

See 6.1 and 6.2.

C.4 Method of test

C.4.1 Procedure

At an appropriate test site or sites, workers potentially exposed to the analyte should be selected, in order to cover as wide a concentration range as practicable, without deliberately exposing workers to concentrations at or around the limit value. For each selected worker, use one diffusive sampler and one sampler of an independent method (see 6.3; preferably that used to verify the calibration gas mixture in 6.4, provided it is suitable for personal monitoring), placing them in the breathing zone as close as practicable to each other, s that they sample from essentially the same atmosphere. At least 20 data-

pairs are required for this test. Analyze the samplers and calculate the apparent exposure concentration for each sampler. For diffusiv samplers use the calculation in 7.5.

C.4.2 Calculations

C.4.2.1 General

Compare the apparent exposure concentration measured by the diffusive sampler with that measured by the independent method. Any suitable statistical test may be used to determine any systematic difference between the two sets of results. Two possible tests are given in C.4.2.2 and C.4.2.3.

C.4.2.2 Paired sample t-test

Construct a table with the data-pair number (i) and the two estimates, x(i) and y(i), of the exposure concentration. In most practical situations, x and y will follow a log-normal distribution, so add columns for log x(i) and log y(i). Add a last column for [log x(i) - log y(i)]. On the assumption that [log x(i) - log y(i)] is normally distributed, calculate the mean and standard deviation and test whether the mean is significantly different from zero by a t-test using 95 % confidence limits.

C.4.2.3 Linear regression analysis

On the assumption that there is a linear relationship between x and y, the relationship between the two sampling methods may be examined by linear regression analysis. It is convenient to use a computer program, and as in C.4.2.2, a logarithmic transformation is desirable in order to normalize the standard deviation of measurements made at different concentrations. The result of a linear regression analysis will normally be the values a and b of the equation:

$$\log y = a + b \cdot \log x \qquad \ldots (C.1)$$

together with standard errors of a and b, and a correlation coefficient, r.

Annex D (informative)

Field tests - Multiple comparisons

D.1 Introduction

Although the diffusive uptake rate will have been determined, and any effect of environmental factors checked in the laboratory tests, there may be some factors existing in the workplace that will influence the performance of a diffusive sampler. Such factors may be rapidly changing concentrations, or the presence of unanticipated interferences, or the presence of the analyte either as suspended matter or sorbed onto suspended matter. Tests should therefore be conducted under conditions typical of the intended use of the diffusive sampler, to determine the precision of replicate sampler results and those of an independent method under these conditions.

D.2 Requirement

The field precision of the diffusive sampler (see D.4.2.1) should not greatly exceed the precisi n determined under laboratory conditions (see 7.13). In deciding whether the field precision is acceptable, the determined value for the independent samplers (see D.4.2.2) needs to be taken into account.

3M Company
3M OH & ES Division
3M Center Bldg 260-3B-09
St Paul , MN 55144-1000

Fax Cover Sheet

DATE **AUGUST 28, 1995**

TO:	Bill Erny	**PHONE:**	703-525-1695
	ISEA	**FAX:**	703-528-2148
FROM:	Bob Weber	**PHONE:**	612-737-4459
	3M Company	**FAX:**	612-736-7344

RE: Appendix on Field Testing

Number of pages including cover sheet: [3]

Message

Hi Bill;

Enclosed is the updated draft for Field Evaluations with diffusion monitors.

Talk to you later. see you in November

Bob Weber, CIH

Senior Technical Service Representative

Bob Weber

Appendix ?

Field Test

Introduction

Laboratory validation of diffusion monitors defines the operating parameters of the device and accounts for many of the variables that may be encountered in the field; however, there may be factors in the workplace that will influence the performance of the diffusion monitor that cannot be anticipated in laboratory validation studies. For example such factors as intermittent and rapidly changing concentrations, or the presence of interference's. Therefore testing the diffusion monitor under actual field conditions is recommended.

Several factors need consideration before conducting field evaluations. First, the true concentration is not known and therefore must be estimated with an independent method. However, the independent method is subject to errors just as the diffusion monitor. Therefore the difference between the two should not be interpreted as a bias. Second, the use of side-by-side sample collection must be carefully monitored. Sampling devices, either active or diffusive, placed on an individual's right and left lapels may give different results; although each may give an accurate measurement of the concentration to which they were exposed. The differences in side-by-side sampling can be attributed to the existence of concentration gradients in the sampling area. Concentration gradients may be due to the individual's location to the contaminant producing equipment or process, direction in which the individual is facing during exposure, and the type of work being performed. Third, the environmental factors in the field must be determined to insure that the diffusion monitor and independent method are being conducted within their operational ranges.

Field Test Methods

Evaluation of diffusion monitors in the field can be conducted by two different sampling techniques. The first technique, personal sampling, involves having individuals wear both the diffusion monitor and independent sampling device simultaneously. This technique is subject to errors outlined earlier. The second technique, field chamber sampling, involves exposing both sampling techniques to an atmosphere of homogenous analyte concentration and a face velocity sufficiently high enough to prevent diffusion monitor starvation. Workplace air is drawn into a chamber where a statistically significant number of sampling devices will simultaneously collect the contaminants. Field chamber sampling may not represent a typical worker exposure, however it does eliminate errors that are associated with personal side-by-side sampling.

Field Chamber Sampling

The field test chamber should be large enough to collect at least 5 sampling pairs simultaneously (one of the independent method and one diffusion monitor). The air flow into the chamber should be sufficient so that face velocity across the surface of the monitor is high enough to prevent starvation. The analyte concentrations in the workplace should be within the working range of both sampling devices. At least 20 sampling data pairs are needed for statistical comparison. Statistical analysis of data should be conducted to assess the difference between the sampling methods.

Personal Sampling

Chose a work site that has a wide range of analyte concentration, but has sufficient concentration in order to collect enough analyte to accurately measure in the laboratory. Each worker selected to participate in the study should wear a pair of sampling devices (one of the independent method and one diffusion monitor). Sampling pairs should be placed in the breathing zone of the worker and as close as practical to each other, if possible they should also be placed on the same lapel of the worker. At least 20 sampling data pairs are needed for statistical comparison. Statistical analysis of data should be conducted to assess the difference between the sampling methods.

a diagram of chamber will be included.

SKC®

Innovation • Quality • Commitment

TO: MEMBERS OF THE ISEA COMMITTEE ON PASSIVE MONITOR (DIFFUSIVE SAMPLER) STANDARDS

8 August 1995

During the month of July, I met with Dr Richard H. Brown of the Health & Safety Executive (U.K.), and Working Group 5 of CEN TC137. The subject of the meeting was the potential for trans-Atlantic harmonization of diffusive sampler standards. The following points came out of the discussion:

1. The CEN Committee TC137 is aware of the work of ISEA and is in favour of harmonization.

2. It was agreed that all protocols for the evaluation of diffusive samplers contained fairly minor variations of essentially the same tests to test the effects of a well-r cognized range of influences on the overall accuracy of the sampler. In view of this it should be possible for the experimental parts of two standards to become compatible.

3. The European protocol is incredibly flexible (more so than I had thought), which allows interpretations favourable to harmonization. Such flexibility is demonstrated by:
a) any test can be excluded based on published justifications, and,
b) any test can be modified to exclude conditions that will not adversely affect the sampler (again, based on published justifications).

4. The European standard can be modified based on the results of future research (for instance, where tests are shown not to be adequate, or where poor test design becomes apparent), and a project to undertake such research has been submitted for European funding.

/cont.

SKC Inc.
863 Valley View Road
Eighty Four, PA 15330, USA
Phone: 412-941-9704
Fax: 412-941-1369

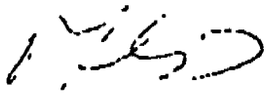
5. Third party certification or auditing is not required for compliance with the European standard.

6. The conditions used in the European standard are designed to be a minimum set of conditions that samplers ought to be able to pass. If an American evaluation happens to select those conditions then it will pass the European standard. If an American evaluation chooses a less stringent range of condition it may still pass the European protocol if a justification as per 3.b can be invoked. If not, it can still be used, but if there is a sampler that more closely passes the minimum conditions, that is the one that must be chosen.

7. The reasons for the accuracy and precision standards needed to pass the European standard 482 are not under current scrutiny and will not likely be relaxed (at 30% they are currently more relaxed than NIOSH) in the near future.

I will be incorporating some of these comments into the parts of the draft standard for which I have responsibility. I hope it will be possible for all of them to be discussed further at the November meeting. This will be very timely since I will be presenting a paper at a meeting in London in December which will be titled "Moves towards standardization in the United States" at which I will be able to discuss these matters further with the CEN personnel.

Best regards, and look forward to seeing you all again,



Martin Harper, PhD
Assistant Research Director, SKC Inc.

Submitted to Skip Elliott (Chairman) for global distribution

Copy to Bill Erny, ISEA
David Bartley, NIOSH/ASTM

for Gas Detector Tube Units –

Short Term Type for Toxic Gases and Vapors in Working Environments

ANSI American National Standards Institute
1430 Broadway
New York, New York
10018

ANSI/ISEA 102-1990

American National Standard

Approval of an American National Standard requires verification by ANSI that the requirements for due process, consensus, and other criteria for approval have been met by the standards developer.

Consensus is established when, in the judgment of the ANSI Board of Standards Review, substantial agreement has been reached by directly and materially affected interests. Substantial agreement means much more than a simple majority, but not necessarily unanimity. Consensus requires that all views and objections be considered, and that a concerted effort be made toward their resolution.

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Published by

American National Standards Institute
1430 Broadway, New York, New York 10018

Printed in the United States of America

A8C990/12

American National Standard
for Gas Detector Tube Units –

Short Term Type for Toxic Gases and Vapors in Working Environments

Secretariat
Industrial Safety Equipment Association

Approved May 25, 1990
American National Standards Institute, Inc

Foreword

(This Foreword is not part of American National Standard ANSI/ISEA 102-1990.)

This standard has been drafted to establish a voluntary standard for gas detector tube units. The standard was developed from the National Institute for Occupational Safety and Health (NIOSH), originally titled 42 Code of Federal Regulation 84–1973. Its use was discontinued in recent years.

The purpose of this standard is to provide a means of continual testing of gas detector tube units and components for accurate performance in working environments, by determining the concentrations of toxic gases and vapors.

This standard was processed and approved for submittal to ANSI by the Canvass Method. The following organizations recognized as having an interest in the standardization of gas detector tube units were contacted prior to the approval of this standard. Inclusion in this list does not necessarily imply that the organization concurred with the submittal of the proposed standard to ANSI.

AFL-CIO
Alliance of American Insurers
American Gas Association
American Industrial Hygiene Association
American Insurance Services Group, Inc
American Iron and Steel Institute
American Mining Congress
American Petroleum Institute
Bituminous Coal Operators Association
Chemical Manufacturers Association
Compressed Gas Association
Edison Electric Institute
Hazardous Material Research Center
Industrial Health Foundation
Industrial Safety Equipment Association
Instrument Society of America
International Brotherhood of Electrical Workers
International Chemical Workers Union
Matheson Gas Products
Mobil Oil Corporation
National Fire Protection Association
National Institute for Occupational Safety and Health
National Safety Council
Occupational Safety and Health Administration
Oil, Chemical and Atomic Workers Union
Sensidyne, Inc
United Auto Workers
United Mine Workers
United Steelworkers
U. S. Deparument of Labor

Suggestions for the improvement of this standard will be welcome. They should be sent to the Industrial Safety Equipment Association, 1901 No. Moore Street, #501, Arlington, VA 22209.

Contents

American National Standard for Gas Detector Tube Units –

Short Term Type for Toxic Gases and Vapors in Working Environments

1. Purpose

This standard sets forth the performance requirements for gas detector tube units and components, which are used to determine the concentrations of toxic gases and vapors in working environments.

2. Referenced Standards

This standard is intended to be used with the following standards:

MIL-STD-105E, 10 May 1989, Military Standard, Sampling Procedures and Tables for Inspection by Attributes[1]

MIL-STD-414, 11 June 1957, Military Standard, Sampling Procedures and Tables for Inspection by Variables for Percent Defective[1]

3. Definitions

batch. A quantity of material defined as *lot* or *batch* in MIL-STD-105D, 1989, and MIL-STD-414, 1957.

component. Any gas detector tube, sampling pump, or other device that changes the nature of the contaminant so that it may be measured by the tube, and is designed to operate as a constituent of the tube unit in such a way that the entire unit meets the requirements of this standard.

contaminant. A specific chemical substance, usually a toxic gas or vapor, appearing in a workplace air environment.

cross-sensitive gas or vapor. A gas or vapor that produces a stain similar to that obtained from presence of the contaminant.

[1] Available from the Government Printing Office, Washington, DC 20402.

expiration date. The date until which tubes from the batch shall meet the requirements of this standard, if stored from time of manufacture according to the storage instructions.

gas detector tube. A tube containing a chemically impregnated material which indicates the concentration of the contaminant or group of contaminants in the air by means of a chemically produced color change. Length-of-stain tubes indicate contaminant concentration by the length of stain formed. Color-comparison tubes indicate concentration by the color or intensity of the stain when compared to measurement standards. Group-type gas detector tube units are those designed and manufactured to measure more than one contaminant.

independent tube reader. A person measuring the length of stain or comparing the color or intensity of stain in a tube unit, in accordance with the instructions furnished by the manufacturer, who is not aided by another person in reading the tube, has no knowledge of other reader results, and has no prior knowledge of the actual contaminant concentration other than from tube unit readings.

interferent gas or vapor. Any gas or vapor that alters the expected stain length, color, or intensity for a given concentration of the contaminant.

manufacturer. An individual, partnership, company, corporation, association, or other organization that designs, manufactures, or assembles, a gas detector tube unit.

MIL-STD. A specific military standards document approved by the U.S. Department of Defense.

operating range. The manufacturer's stated overall range of measurements for the contaminant. The operating range of the gas detector tube unit may exceed the test standard range.

shall. The word *shall* denotes a mandatory requirement.

should. The word *should* denotes a recommendation.

test standard. The contaminant concentration in air that is the current Adopted Value TLV® published at the time of certification by the American Conference of Governmental Industrial Hygienists (ACGIH), for each contaminant for the purpose of defining the minimum concentration range to be measured by the tube.

test standard range. 0.5 to 5 times the test standard concentration of the contaminant expressed in terms of parts per million (ppm) or percent by volume or other appropriate unit of measure.

tube unit. A device for measuring or signaling the presence of one or more gaseous contaminants in the atmosphere of a working environment, which consists of a gas detector tube and a sampling pump, and which may also include a sample conditioning tube or pyrolyzer or any other components required for proper functioning of the gas detector tube, or any other device, such as an automatic stroke counter, which enhances the convenience or usability of the tube unit. The tube unit as defined herein consists only of components supplied by the same manufacturer.

4. Required Information

4.1 Each component or set of components shall include instructions stating the additional components with which it has been manufactured for use as a tube unit meeting the requirements of this standard.

4.2 Each sampling pump shall be accompanied by instructions that shall enable the user to verify by a simple field test the capability for accurate flow rate or proper time to fill the pump to full volume, and to verify the absence of leakage. Instructions shall also be provided for making simple corrective adjustments to the pump and for replacing minor parts.

4.3 Each box of gas detector tubes shall be labeled with the following minimum information:

(1) Identification of the contaminant or contaminants for which the tubes were manufactured and designed to measure

(2) Test standard range

(3) The expiration date of the tubes

(4) Manufacturer name, part number, and batch number

(5) Storage instructions

(6) Batch number of sample conditioning tube or applicable device, if included in box of gas detector tubes, and if different from gas detector tube batch number

4.4 If the operating range is stated on the label it shall be clearly differentiated from the test standard range.

4.5 Each box of gas detector tubes shall be accompanied by the following information:

(1) Instructions detailing the measuring procedure using the gas detector tubes, sampling pump, and any required components.

(2) Instructions for obtaining contaminant concentration values from tube readings.

(3) The temperature, pressure, and humidity at which the tube has been calibrated, and methods for quantitatively correcting tube readings necessitated by use of the tubes at conditions of temperature, pressure, and humidity other than those at which the tube was calibrated.

(4) Limitations of the tube unit in obtaining accurate concentration measurements, including a list of known interferent or cross-sensitive gases or vapors.

(5) Basic chemical reactions involved in the operation of the tube, including the chemical composition of the reagent with which the contaminant reacts and the end products resulting from the chemical reactions, if known. Where such information is a trade secret, such information need not be set forth.

(6) For length-of-stain type detector tubes only, each box of tubes shall be accompanied by a calibration chart or curve showing those concentrations of each contaminant that the tube measures which correspond to various stain lengths. Alternatively, the chart or curve or other calibration markings may appear directly on, or as part of, each tube. The calibration shall be based upon the method described in 5.4.

(7) For color-comparison type detector tubes only, each box of tubes shall be accompanied by a color chart showing those concentrations of each gas the tube measures, that correspond to various color changes of the indicating reagent section of the detector tube, and to the volumes of the air sampled. The calibration shall be based upon the method described in 5.4.

(8) Each sampling pump, pyrolyzer, or other component not packaged inside a box of detector tubes must be identified by a serial number or other means of identification so that the date or batch number of manufacture, or both, may be ascertained.

5. Construction and Performance Requirements

5.1 General

5.1.1 The accuracy of gas detector tube units shall be such that measurements made by these units, when

used in accordance with the manufacturer's instructions, produce measurements of contaminant concentrations with ±25 percent of the actual value at concentrations of 1, 2, and 5 times the test standard of the contaminant, and within ±35 percent of the actual value at a concentration of one-half the test standard.

5.1.2 Gas detector tubes shall continue to meet the performance requirements of this standard from the date of manufacture until the expiration date, if the tubes are stored according to the manufacturer's instructions during the elapsed time.

5.2 Length-of-Stain Type Detector Tubes

5.2.1 In addition to requirements stated in 5.1, length-of-stain type detector tubes shall produce either of the following:

(1) A minimum length of stain such that the calibration point on the calibration chart or curve for a concentration equal to the test standard for the contaminant shall correspond to a stain length of 15 mm or greater

(2) At a concentration equal to the test standard for the contaminant, produce a stain with such a clear and sharp end point that the following requirement is met:

$$\frac{s}{\bar{x}} \leq 0.10$$

where:

s = The standard deviation of the tube readings obtained from three or more independent tube readers when reading an individual stained tube

$\bar{x}$ = Mean value of the tube readings

5.2.2 Channeling of airflow through the detector tube shall be minimized so that the maximum variation of stain length around the circumference of the tube at the interface between stained and unstained reagent shall be such that:

$$\Delta \frac{L}{M} \leq 0.20$$

$$\Delta L = L_2 - L_1$$

where:

L_2 = The concentration value indicated by the length of stain at the side of the tube where the stain is farthest extended along the tube's longitudinal axis.

L_1 = The concentration value indicated by the length of stain at the side of the tube where the stain is least extended along the tube's longitudinal axis.

M = The mean value between L_2 and L_1

5.2.3 Gas detector tubes should be assembled so that the zero point formed by the surface of the indicating material is perpendicular to the longitudinal axis of the tube. If this interface is not perpendicular, the maximum variation shall not be greater than 2 mm along the longitudinal axis of the tube.

5.3 Color-Comparison Type Detector Tubes. In addition to requirements stated in 5.1, color-comparison type detector tubes shall meet either of the following requirements:

(1) Color charts and sampling volume combinations shall be provided for concentrations of 0, 0.5, 1, 2, and 5 times the test standard. Additional color charts and sampling volume combinations shall be provided if necessary to meet the minimum performance requirements of 5.1.

(2) A sufficient number of color charts and sampling volume combinations shall be provided so that the following requirement is met when readings are obtained by interpolation between color comparison charts:

$$\frac{s}{\bar{x}} \leq 0.10$$

where:

s = The standard deviation of the tube readings obtained from three or more independent tube readers when reading an individual stained tube

$\bar{x}$ = Mean value of the tube readings

5.4 Calibration

5.4.1 Gas detector tubes from each batch of tubes shall be tested by the manufacturer for accuracy of contaminant concentration measurement, by using the tubes to sample known concentration of contaminants.

5.4.2 Correction factors for temperature, relative humidity, pressure, and other pertinent variables shall be applied to the tube readings before evaluating such readings for accuracy.

5.4.3 Routine calibration of each batch of tubes by the manufacturer shall be conducted at ambient room temperature in the range of 65-85° F (18.3-29.5°C). Relative humidities shall be adjusted to approximately 50 percent, except for cases in which the presence of a substantial amount of water vapor would result in unstable contaminant concentrations, interfere with concentration monitoring systems, or otherwise cause a disturbance of test conditions. In such cases, a lower relative humidity may be used.

5.4.4 The manufacturer shall perform tube calibration tests on gas detector tubes from each batch of its tubes, at concentrations of 0.5, 1, 2, and 5 times the test standard for the contaminant.

To ensure acceptable performance over the full operating range, the manufacturer should perform adequate tube calibration tests on detector tubes from each batch of its tubes at suitable concentrations over the operating range.

5.4.5 Calibration concentrations shall be generated using one of the following methods:

(1) A dynamic contaminant generation system, as by a gas saturating method (employing the vapor pressure of the substance), permeation tube devices, or other instruments or devices which generate gases at a steady, measurable rate

(2) An analyzed gas mixture from a pressurized cylinder

(3) A static concentration system prepared by injecting a known mass of liquid contaminant into a sealed container of known volume, and allowing time for evaporation and the equilibration of adsorption and desorption on container walls

5.4.6 Independent chemical or physical analysis shall be used to verify the test concentration of the gas generated, according to 5.4.5, except in the case when no independent method of acceptable accuracy has been developed.

5.4.7 The manufacturer shall periodically test gas detector tubes in the presence of interferent or cross-sensitive gases to verify the stated interferent or cross-sensitivity levels, and to determine what additional gases might also interfere or be cross-sensitive with detector tube readings, and to what degree such interferences or cross-sensitivities might occur.

6. Sampling Pumps

6.1 Sampling pumps for drawing the air to be sampled with detector tubes shall be free from leakage that can result in erroneously low tube readings, and shall be calibrated to sample at whatever flow rate or rates or time to fill the pump to full volume are deemed appropriate by the manufacturer, in order to assure accurate measurements.

6.2 Leakage shall not exceed 3 percent of the pump's single stroke volume per minute. This is tested by evacuating the pump and plugging the pump inlet with an unopened detector tube from the tube unit being tested.

6.3 Pumps shall be calibrated by the manufacturer to insure that they are capable of sampling accurately the stated volume at the stated flow rate. Subsequent to a check of proper flow rate and volume, the pump shall be capable of drawing 100 full-capacity strokes of air without deviating more than ±10 percent from the calibration flow rate, and without deviating more than ±5 percent from stated pump volume.

6.4 Flow control devices, if used, shall regulate the flow rate to within ±10 percent of the rate stated by the manufacturer for each flow rate control device.

6.5 To ensure that air samples do not backflow into detector tubes from the pump, the performance of the discharge check valve system shall be such that when 10 consecutive pump strokes are taken, the total volume of air drawn into the pump through its inlet, minus the total volume discharged through the pump inlet (or outlet if pump design mandates), shall be within 5 percent of 10 times the pump's volume capacity for a single stroke.

7. Quality Assurance

7.1 **Sampling Plan.** The sampling plan shall include a list of the characteristics to be measured, inspected, or tested. These characteristics shall be classified according to the potential effect of each nonconformance and grouped into the following classes:

(1) *Special.* Tube reading accuracy.

(2) *Critical.* A nonconformance that will make the gas detector tube unit completely inoperative or render it unusable for its intended purpose.

(3) *Major.* A nonconformance other than critical, that is likely to result in failure, or reduce materially the usability of the gas detector tube unit in its intended purpose.

(4) *Minor.* A nonconformance that is not likely to reduce materially the usability of the gas detector tube unit for its intended purpose, or is a departure from established standards having little bearing on the effective use or operation of the gas detector tube unit.

7.2 **Acceptable Quality Level.** The acceptable quality level (AQL) for each special, critical, major or minor nonconformance, so classified by the manufacturer, shall be as follows:

(1) *Special.* 6.5 percent.

(2) *Critical.* 1.0 percent where tests are destructive. For non-destructive tests, see 6.3.

(3) *Major.* 2.5 percent.

(4) *Minor.* 4.0 percent.

For critical characteristics and where tests are non-destructive, each item manufactured shall be 100 percent inspected for nonconformances, and all nonconforming items shall be rejected.

7.3 **Inspection Levels.** Inspection level II as described in MIL-STD-414, 1959, shall be used for special characteristics and destructive tests for critical characteristics, except when an equivalent inspection level is utilized. Inspection level II as described in MIL-STD-105D, 1989, or inspection level IV as described in MIL-STD-414, 1959, shall be used for major and minor characteristics, except when an equivalent inspection level is utilized.

Appendix (This Appendix is not part of American National Standard ANSI/ISEA 102–1990, but is included for information only.)

Recommendation and Precaution concerning Gas Detector Tube Unit Use

Since the indicating behavior of a detector tube depends not only on the stroke volume, but also on the suction characteristic of the pump, it must be ensured that each detector tube is used only with the prescribed pump. Pump and tube and components are designed, manufactured, and calibrated together to form a gas detector tube unit. User interchange of pumps and tubes or components supplied by different manufacturers may provide erroneous and invalid measurements of toxic environments. Accordingly, such interchange is *not* recommended.

Internal Correspondence

3M

Occupational Health and Environmental Safety Division

To: R.J. Haggerty - OH&ESD - 275-6W-01
R.E. King - OH&ESD - 260-3B-09

From: R.A. Weber (7-4459) - OH&ESD - 260-3B-09

Subject: **ISEA INSTRUMENT & GROUP MEETINGS**

Date: June 2, 1995

The ISEA Instrument group had two meetings during the AIHC. The first meeting involved the subcommittee working on the diffusion monitor protocol and the second was the entire instrument group.

Review of Diffusion Monitor Subcommittee Meeting

The following people were in attendance: Skip Elliott - Environmetrics, Gus Manning - Assay Technology, Lawrence Locker - Advanced Chemical Sensors, Katie Spear - MSA, Bob Curtis - OSHA, Martin Harper - SKC, Stephen Zlocysti - MSA (Auer).

The group elected officers; Skip Elliott was elected chairman and I was elected vice-chairman.

Stephen Zlocysti, chairman of the CEN committee working on the European diffusion monitor standard gave our group an update on their standard prEN838. This standard is now out for votes and he expected it to be a final standard by the end of the year.

Since our last meeting in February, the group has been very active in writing the standard. We reviewed the draft document during this session and in general, we had some lively discussions. Some of the issues involved the following:

1. The types of devices that this standard should cover. Presently, we have settled on three classifications.

2. We discussed the evaluation criteria and we ended up with a consensus on what types of tests need to be conducted. Specifics on sample sizes and testing levels are still open for further discussion. We agreed that we will not include pressure in evaluation criteria and we also agreed that factorial designed experiments may be run as an option.

3. We agreed that the document should contain language or guidance on field evaluations.

4. The document will contain recommendations for manufacturers. This section will include information on quality control programs and labeling.

5. We decided that ±25% accuracy would not be a requirement. Accuracies only need to be determined and started.

Each member of the committee has specific sections to develop. Draft sections need to be submitted by the end of July. In August the document will be sent out for committee review. If committee finds this draft acceptable, we will then distribute to a field of experts for their comments. These comments will then be reviewed at our next committee meeting. We are scheduled to meet again during the National Safety Congress.

Instrument Group Meeting

The members of this group are mainly concerned about direct reading instruments. All of the major players in the business are participants in ISEA. Following is a list of items that the committee is actively involved with: ANSI Standard on Detector Tubes, ISA O_2 Standard, NFPA306, CEN Instrument Standards, ANSI Z-117 Confined Space Standard, OSHA 1910.134 and writing an ANSI Diffusion Monitor Protocol.

Although we presently do not have a product that fits into the direct reading sensor market, the meeting gave me an understanding of issues that our competition is dealing with.

Summary

I walked away from this meeting realizing that there is a maze of instrument and sensor standards that we need to better understand if we ever plan to enter this market. My major objectives in working with this ISEA committee is to assist in writing the ANSI Diffusion Monitor Protocol and to learn about the standards and issues of gas and vapor detection instruments.

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DATE: 12-14-95

TO: BOB WEBER	YOUR FAX NUMBER: 1-612-736-7344
COMPANY: 3M Co.	REFERENCE:
FROM: GUS MANNING	SEE BELOW/ATTACHED

This is page ONE of 1 Pages. If you do not receive all pages, please call 1-800-833-1258.

Dear Bob... At our recent meeting of the Diffusive Sampler standard committee I was asked to work on the material you provided with respect to Field Testing. I agreed with every word you wrote and only sought to reduce the number of words and, perhaps, to sharpen the focus a little. Please review what I have done and provide some feedback either to myself or directly to Bill Erny at ISEA.

- Best Regards... Gus Manning

Gus

Field Testing

While environmental factors affecting the accuracy of Diffusive Air Sampling Devices are described and studied in the Evaluation Program, factors which may affect accuracy in particular workplaces may be difficult to include in studies which can be reasonably conducted by device manufacturers or third party evaluators. Workplace-specific factors may include fluctuations in temperature, humidity, etc., beyond ranges studied, and, especially, the presence of substances which may overload the sampling device or interfere with the analysis of contaminants.

The validation of Air Sampling Devices subject to such factors is generally believed to be accomplished by field testing. While field studies have the advantage of utilizing actual workplace conditions, they also have disadvantages, as follows.

(1) Field conditions may not allow the analyst to present sufficient reference devices to uniform contaminant concentrations to establish statistically valid reference values for comparison to the devices being tested.

(2) Field conditions in a particular study may not reflect typical field conditions for the workplace being studied.

(3) Field conditions in a particular field study may not be applicable to other workplaces.

In summary, field testing is recommended as a desirable supplement to the Standard which can determine the suitability of a generally validated Air Sampling Device for a specific workplace.

Since field conditions existent in a particular workplace may not represent other workplaces, specific field testing requirements are not included in this standard which is developed for the general evaluation of devices. Further, field testing is not viewed as a replacement for the tests described under Evaluation Program.

May 2, 1995

VALIDATION OF DIFFUSION MONITORS

SLIDE 1 (Title)

Validation of Diffusion Monitors. R.A. Weber, and D.J. Larsen, 3M Occupational Health and Environmental Safety Division, 3M Center, Building 260-3B-09, St Paul 55144

SLIDE 2 (Picture)

Diffusion monitors utilize the natural phenomena of diffusion to collect gases & vapors. Diffusion monitors have undergone extensive evaluations by the scientific community since their introduction in the late 1970's. Some of these evaluations have been comparison studies with reference sampling methods such as charcoal tubes and pumps while other evaluations have included the development of large validation protocols. Today I would like to talk about some of those protocols, plus I would like to present a newly developed 3M protocol that includes many aspects reviewed in other works. 3M has always conducted validation studies of their diffusion monitors, but with this new protocol we are standardizing our testing techniques.

SLIDE 3

A validation protocol specifies performance criteria that needs to evaluated. It should also include specific testing conditions, such as chamber exposure concentrations and sampling times. It may also reference sample sizes and the type of statistics that should be used to evaluate the critera.

One goal of a protocol is to define the limitations of the sampling device. This is an important aspect that is sometime overlooked. For example, one type of diffusion monitor may not sample accurately for 8 hours at 2 times the PEL for benzene, however it may be very accurate at sampling the STEL for benzene. The protocol should find those performance limits and outline them so the user can understand the boundaries in which they operate.

SLIDE 4

Most diffusion monitor validation studies agree on one thing that is the performance criteria that should be studied, such as, desorption efficiency, humidity, sampling rate, reverse diffusion, storage, face velocity, temperature, orientation and the relationship of concentration and time.

SLIDE 5

Since the introduction of diffusion monitors there have been numerous published and un published protocols. Manufacturers, laboratories, NIOSH, the European Community and now possibly the Industrial Safety Equipment Associate (ISEA) have all taken their turns in developing validation protocols.

SLIDE 6

In the late 1970's 3M and DuPont were involved in the development of diffusion monitors, including setting of performance critera for evaluating accuracy. They realized that diffusion monitors like all other sampling devices do have limitations and they recognized that those limits needed to be investigated. Recently other manufacturers of diffusion monitors have also published information on methods. For example SKC has developed a bi-level validation approach, this technique evaluates performance of diffusion monitors for classes of compounds.

SLIDE 7

Laboratories throughout the world have been involved in evaluating diffusion monitors since their introduction. Much of the evaluation work has been published in peer reviewed journals. Exxon, Abbot Laboratories and Goodyear have all conducted validation studies and while the studies were designed differently they looked at many of the same performance critera.

In 1984 Brown et. al, at the Occupational Hygiene Laboratory published a paper titled "A Diffusive Sampler Evaluation Protocol." This work evaluated many of previously mentioned performance criteria, however instead of looking at each separately, factorial experiments were designed to look at the interaction of performance criteria.

SLIDE 8

In the late 1970's when diffusion monitors were introduced NIOSH took an active role in assisting in the development of guidelines for their evaluation. In 1987 NIOSH published a protocol intended as a guideline for manufactures and others to follow to evaluate diffusion monitors. This document has created allot of confusion in the industrial hygiene environment because some people have viewed this document as a standard instead of a guidance document. The protocol outlines many of the performance critera mentioned earlier, however NIOSH took the program one step further and recommended a complex 16 run factorial designed experiment. The protocol also included sample sizes for each experiment. In order to implement this protocol for a single chemical it would take in excess of 200 diffusion monitors. Because of the cost and complexity of the protocol it has never been fully accepted in the industrial hygiene community.

SLIDE 9

The European Community for Standardization (CEN) has developed a protocol for diffusion monitors. The goal of the standard is a consistent procedure for manufactures and users to follow for evaluating diffusion monitors. Presently the protocol prEN 838 is in the draft stage. It addresses the same performance critera that has already been previously mentioned.

SLIDE 10

At the request of OSHA the Industrial Safety Equipment Association (ISEA) and the Safety Equipment Institute (SEI) were asked to become involved in writing a ANSI sponsored validation protocol and developing a certification program for diffusion monitors. This process and program would be very similar to what has been developed and implemented with detector tubes. The program has just begun and a timetable for completion has not been established.

SLIDE 11

Consensus among manufactures and users is that diffusion monitors should undergo a laboratory evaluation prior to use in the field. Unfortunately to date a standardized evaluation program or validation protocol has never been agreed upon, therefore there many validation studies done over the years all have been designed differently. As a result there has been confusion about the performance of diffusion monitors. We believe the objectives of properly designed protocol are as follows:

1. Show the operating limits of the device
2. Evaluate desorption efficiency, reverse diffusion, storage, sampling rate, humidity, air velocity and the relationship between concentration and exposure time.
3. Can be utilized by others
4. Specify Testing Conditions
5. Results of validation are meaningful and they can be easily shared with the user, such as the industrial hygienist.

While we wait for the ISEA/ANSI document to become a reality 3M has decided to implement their own standardized diffusion monitor protocol, in which the information can be easily passed along the end user.

I would like to now review our protocol

SLIDE 12

The first performance criteria to be evaluated in the validation study should be desorption efficiency. Recoveries will vary depending on the affinity of the analyte to the sorbent, solubility of the anlayte in the desorbing agent and the mass of analyte collected. The most wildly used solvent today is carbon disulfide, however alternative sorbents should be investigated if recoveries are below 75%. Possible alternatives are methylene chloride and acetonitrile. Some recent work by the OSHA Salt Lake City Laboratory has revealed that a mixture of CS2 and dimethylforamide (DMF) results in excellent recoveries with polar compounds.

SLIDE 13

Our desorption efficiency study consists of analyzing three sets of four monitors at a mass levels that represent eight hour exposures at 0.1 EL, 0.5 EL and 1.0 EL. NOTE:EL refers to the exposure level, it could represent the TLV or PEL or another appropriate standard. If the mean recoveries are greater than 75 % and the coefficient of variation is , <.1 then the recovery solvent is acceptable.

SLIDE 14

The following results were obtained by desorbing monitors with carbon disulfide. The data indicates for the mass levels between 0.1 to 1.0 EL for 8 hours - you could expect recoveries > 85%. Therefore the CS2 is an appropriate desorbing solvent for methylene chloride and toluene.

SLIDE 15

Humidity will influence collection of gas & vapor contaminants with diffusion monitors because water will compete for active sites on the sorbent. This set of tests will investigate the relationship between relative humidity and capacity. Results can also be used to determine the sampling rate of the diffusion monitor.

SLIDE 16

The test method utilizes 12 diffusion monitors. Monitors are exposed to 1 EL at a RH of 50%. 3 monitors are removed after 2 hours, 4 hours 6 hours and 8 hours.. Next the experiment is repeated at 80% RH.

SLIDE 17

To interpret the results compare the derived sampling rates for the 50% RH and the 80% RH and 2 and 4 hour sampling times, this is referenced as cells 1,2,5, and 6, if results are statistically the same it shows that monitors can be used up to four hours. Next compare the 50% and 80% RH, 6 and 8 hour sampling rates, cells 3,4,7 and 8 with the previous calculated rates. If these are statistically the same it shows that the monitors can be used up to 1 EL for 8 hours.

The table shows that the toluene sampling rate at 50% and 80% RH's for the 2 to 8 hour sampling times are the same, therefore the sampling rate then can be determined from cells 1 -8.

SLIDE 18

The linear sampling rate of Toluene over these conditions can also be seen graphically by comparing the mass collected vs the sampling time.

SLIDE 19

Reverse diffusion is defined as the loss of analyte that had been previously been adsorbed on the sorbent. Sorbents will have a finite capacity for gas & vapor analytes and this capacity may be reduced as environmental influences are introduced, such as other analytes or water vapor from high humidity.

SLIDE 20

To evaluate reverse diffusion , 12 monitors were exposed to 2 EL for 30 minutes at 80% RH. After 30 minutes 6 monitors were removed and analyzed and the other 6 monitors are exposed to clean 80% RH air for an additional 450 minutes. The sampling rate means from each set are compared. Ideally reverse diffusion should be less than 10%. Losses >10% may indicate the need for a monitor with a back-up section or sampling times < 8 hours

SLIDE 21

This graph shows that under experimental conditions the loss by reverse diffusion for both toluene and methylene chloride is <10%.

SLIDE 22

The next performance criteria that is evaluated is the relationship between concentration and sampling time. These experiments will define the uniformity of the sampling rate over a range of exposure times and exposure concentrations. This technique was outlined by Brown, et al in 1984 and as you will see it will provide a sampling performance matrix with respect to concentration and time.

SLIDE 23

The two factorial design consists of nine separate experiments. This test can be performed in two steps. First, six diffusion monitors are exposed to conditions outlined in cells 1,3,7 and 9. Sampling rates from each experiment are determined. Cells 1,3,7 and 9 show the outer operating boundaries of the device. The accuracy of the sampling and analytical method can then be determined by using the sampling rate derived from the humidity experiments or from a previously published sampling rate.

If accuracy's in cells 1,3,7 and 9 are not acceptable then accuracy's can be determined in the remaining cells.

Exposure conditions outlined in the cells will have to vary from compound to compound, this is because as EL's get lower it becomes more difficult to generate test atmospheres and it becomes difficult to collect enough mass for analysis, therefore the accuracy determined in cells 1 and 3 may be greatly influenced by these conditions.

SLIDE 24

The following is an example of this experiment. It shows the operating accuracy's of the an OVM for sampling toluene. The EL for this experiment was 100 ppm and a SR of 31.4 cc/min. was used as the reference to determine accuracy's.

SLIDE 25

As noted earlier the sampling rate can be determined experimentally in the humidity studies However sampling rates can also be obtained theoretically by using the diffusion coefficients determined by the Hirsfelder equation and the empirical relationship defined by studying classes of compounds such as ketones, alcohols, aliphatics, esters, cellosolves, aromatics and halogens.

SLIDE 26

The following graph shows the sampling rate as a function of diffusion coefficient for 14 different halogenated compounds. The diffusion coefficient in cm2/ sec for methyl chloride is .1102 and by using the regression line the theoretical sampling rate for methylene chloride 37.9 cc/min. The sampling rate obtained empirically by our latest humidity studies indicates a sampling rate of 37.4

SLIDE 27

Prolonged storage of diffusion monitors between exposure and analysis can potentially lead to errors. This experiment investigate loss of analyte after collection. Plus it also investigates room temperature storage vs refrigeration storage.

SLIDE 28

Air velocity and orientation is also included in our validation program. The purpose of this experiment is to determine the minimum face velocity that is required and to evaluate the affects that orientation has on sampling rate.

SLIDE 29

The final criteria in our validation protocol investigates the influence of temperature on the sampling rate.

SLIDE 30

Sampling gases & vapors with diffusion monitors offers many advantages over active sampling with a pump and sorbent tubes. The simplicity of monitors makes the task of characterizing the workplace environment much easier for the industrial hygienist. However the user of the monitor needs to understand the limits or operating boundaries of the device. All diffusion monitors operate based on Fick's law, but because of different geometry's and sorbents the operating boundaries will vary for each. In order for the user to compare monitors it is important that a standardized testing protocol be developed and utilized.

The standardized technique must be practical and realistic to implement. The task of validating monitors for the hundreds of organic compounds is too great of a burden for manufacturers to undertake. Therefore private analytical laboratories may have to conduct their own validation studies.

In 1992 Guild et al, proposed a bi-level validation. This approach involves validating a monitor to classes of compounds. The assumption in this technique is that if you can show the operational boundaries for the most demanding anlayte of a chemical class then you can assume the monitor will operate within the those same boundaries for less demanding analytes in that chemical class.

In order to fully evaluate the performance of a diffusion monitor it also needs to undergo field evaluation. Environmental conditions cannot be fully duplicated in the laboratory. Therefore any type of diffusion monitor validation program should contain some guidance on how to evaluate in the field.

VALIDATION OF DIFFUSION MONITORS

Presented at the 1995 American Industrial Hygiene Conference & Exposition

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The European Community for Standardization (CEN) has developed a protocol for diffusion monitors. The goal of the standard is a consistent procedure for manufactures and users to follow for evaluating diffusion monitors. Presently the protocol prEN 838 is in the draft stage. It addresses the same performance critera that has already been previously mentioned.

SLIDE 10

At the request of OSHA the Industrial Safety Equipment Association (ISEA) and the Safety Equipment Institute (SEI) were asked to become involved in writing a ANSI sponsored validation protocol and developing a certification program for diffusion monitors. This process and program would be very similar to what has been developed and implemented with detector tubes. The program has just begun and a timetable for completion has not been established.

SLIDE 11

Consensus among manufactures and users is that diffusion monitors should undergo a laboratory evaluation prior to use in the field. Unfortunately to date a standardized evaluation program or validation protocol has never been agreed upon, therefore there many validation studies done over the years all have been designed differently. As a result there has been confusion about the performance of diffusion monitors. We believe the objectives of properly designed protocol are as follows:

1. Show the operating limits of the device
2. Evaluate desorption efficiency, reverse diffusion, storage, sampling rate, humidity, air velocity and the relationship between concentration and exposure time.
3. Can be utilized by others
4. Specify Testing Conditions
5. Results of validation are meaningful and they can be easily shared with the user, such as the industrial hygienist.

While we wait for the ISEA/ANSI document to become a reality 3M has decided to implement their own standardized diffusion monitor protocol, in which the information can be easily passed along the end user.

I would like to now review our protocol

SLIDE 12

The first performance criteria to be evaluated in the validation study should be desorption efficiency. Recoveries will vary depending on the affinity of the analyte to the sorbent, solubility of the anlayte in the desorbing agent and the mass of analyte collected. The most wildly used solvent today is carbon disulfide, however alternative solvents should be investigated if recoveries are below 75%. Possible alternatives are methylene chloride and acetonitrile. Some recent work by the OSHA Salt Lake City Laboratory has revealed that a mixture of CS2 and dimethylforamide (DMF) results in excellent recoveries with polar compounds.

SLIDE 13

Our desorption efficiency study consists of analyzing three sets of four monitors at mass levels that represent eight hour exposures at 0.1 EL, 0.5 EL and 1.0 EL. NOTE:EL refers to the exposure level, it could represent the TLV or PEL or another appropriate standard. If the mean recoveries are greater than 75 % and the coefficient of variation is , <.1 then the recovery solvent is acceptable.

SLIDE 14

The following results were obtained by desorbing monitors with carbon disulfide. The data indicates for the mass levels between 0.1 to 1.0 EL for 8 hours - you could expect recoveries > 85%. Therefore the CS2 is an appropriate desorbing solvent for methylene chloride and toluene.

SLIDE 15

Humidity will influence collection of gas & vapor contaminants with diffusion monitors because water will compete for active sites on the sorbent. This set of tests will investigate the relationship between relative humidity and capacity. Results can also be used to determine the sampling rate of the diffusion monitor.

SLIDE 16

The test method utilizes 12 diffusion monitors. Monitors are exposed to 1 EL at a RH of 50%. 3 monitors are removed after 2 hours, 4 hours 6 hours and 8 hours.. Next the experiment is repeated at 80% RH.

SLIDE 17

To interpret the results compare the derived sampling rates for the 50% RH and the 80% RH and 2 and 4 hour sampling times, this is referenced as cells 1,2,5, and 6, if results are statistically the same it shows that monitors can be used up to four hours. Next compare the 50% and 80% RH, 6 and 8 hour sampling rates, cells 3,4,7 and 8 with the previous calculated rates. If these are statistically the same it shows that the monitors can be used up to 1 EL for 8 hours.

The table here shows that the toluene sampling rate at 50% and 80% RH's for the 2 to 8 hour sampling times are the same, therefore the sampling rate then can be determined from cells 1 -8.

SLIDE 18

The linear sampling rate of Toluene over these conditions can also be seen graphically by comparing the mass collected vs the sampling time.

SLIDE 19

The humidity experiment was run with methylene chloride. Results indicate that the 2, 4 and 6 hour sampling rates are statistically the same. Represented in cells 1,2,3,5,6 and 7. The 8 hour sampling rates in cells 4 and 8 are statistically different. Conclusion form this experiment is that if you sample . 6 hours the accuracy will begin to be affected, especially at 80% RH.

SLIDE 20

Reverse diffusion is defined as the loss of analyte that had been previously been adsorbed on the sorbent. Sorbents will have a finite capacity for gas & vapor analytes and this capacity may be reduced as environmental influences are introduced, such as other analytes or water vapor from high humidity.

SLIDE 21

To evaluate reverse diffusion , 12 monitors were exposed to 2 EL for 30 minutes at 80% RH. After 30 minutes 6 monitors were removed and analyzed and the other 6 monitors are exposed to clean 80% RH air for an additional 450 minutes. The sampling rate means from each set are compared. Ideally reverse diffusion should be less than 10%. Losses >10% may indicate the need for a monitor with a back-up section or sampling times < 8 hours

SLIDE 22

This graph shows that under experimental conditions the loss by reverse diffusion for both toluene and methylene chloride is <10%.

SLIDE 23

The next performance criteria that is evaluated is the relationship between concentration and sampling time. These experiments will define the uniformity of the sampling rate over a range of exposure times and exposure concentrations. This technique was outlined by Brown, et al in 1984 and as you will see it will provide a sampling performance matrix with respect to concentration and time.

SLIDE 24

The two factorial design consists of nine separate experiments. This test can be performed in two steps. First, six diffusion monitors are exposed to conditions outlined in cells 1,3,7 and 9. Sampling rates from each experiment are determined. Cells 1,3,7 and 9 show the outer operating boundaries of the device. The accuracy of the sampling and analytical method can then be determined by using the sampling rate derived from the humidity experiments or from a previously published sampling rate.

If accuracy's in cells 1,3,7 and 9 are not acceptable then accuracy's can be determined in the remaining cells.

Exposure conditions outlined in the cells will have to vary from compound to compound, this is because as EL's get lower it becomes more difficult to generate test atmospheres and it becomes difficult to collect enough mass for analysis, therefore the accuracy determined in cells 1 and 3 may be greatly influenced by these conditions.

SLIDE 25

The following is an example of this experiment. It shows the operating accuracy's of the an OVM for sampling toluene. The EL for this experiment was 100 ppm and a SR of 31.4 cc/min. was used as the reference to determine accuracy's.

SLIDE 26

The same experiment was run with methylene chloride. Results indicate a range of accuracy's. Note cell 3, the accuracy at 2.5 ppm for 8 hours was 26.6%. This result is larger then the others not because of performance of the device, but because of the difficulty in generating a 2.5 ppm test atmosphere. Also note cell 9, this test was run at 50 ppm for 8 hours. Earlier I indicated that sampling . 6 hours will influence accuracy and this experiment shows the degree of influence.

SLIDE 27

As noted earlier the sampling rate can be determined experimentally in the humidity studies However sampling rates can also be obtained theoretically by using the diffusion coefficients determined by the Hirsfelder equation and the empirical relationship defined by studying classes of compounds such as ketones, alcohols, aliphatics, esters, cellosolves, aromatics and halogens.

SLIDE 28

The following graph shows the sampling rate as a function of diffusion coefficient for 14 different halogenated compounds. The diffusion coefficient in cm2/ sec for methyl chloride is .1102 and by using the regression line the theoretical sampling rate for methylene chloride 37.9 cc/min. The sampling rate obtained empirically by our latest humidity studies indicates a sampling rate of 37.4

SLIDE 29

Prolonged storage of diffusion monitors between exposure and analysis can potentially lead to errors. This experiment investigate loss of analyte after collection. Plus it also investigates room temperature storage vs refrigeration storage.

SLIDE 30

Air velocity and orientation is also included in our validation program. The purpose of this experiment is to determine the minimum face velocity that is required and to evaluate the affects that orientation has on sampling rate.

SLIDE 31

The final criteria in our validation protocol investigates the influence of temperature on the sampling rate.

SLIDE 32

Sampling gases & vapors with diffusion monitors offers many advantages over active sampling with a pump and sorbent tubes. The simplicity of monitors makes the task of characterizing the workplace environment much easier for the industrial hygienist. However the user of the monitor needs to understand the limits or operating boundaries of the device. All diffusion monitors operate based on Fick's law, but because of different geometry's and sorbents the operating boundaries will vary for each. In order for the user to compare monitors it is important that a standardized testing protocol be developed and utilized.

The standardized technique must be practical and realistic to implement. The task of validating monitors for the hundreds of organic compounds is a great undertakeing, therefore private analytical laboratories and manufacturers may both have to conduct their own validation studies.

In 1992 Guild et al, proposed a bi-level validation. This approach involves validating a monitor to classes of compounds. The assumption in this technique is that if you can show the operational boundaries for the most demanding anlayte of a chemical class then you can assume the monitor will operate within the those same boundaries for less demanding analytes in that chemical class.

In order to fully evaluate the performance of a diffusion monitor it also needs to undergo field evaluation. Environmental conditions cannot be fully duplicated in the laboratory. Therefore any type of diffusion monitor validation program should contain some guidance on how to evaluate in the field.

Validation of Diffusion Monitors

R.A. Weber and D.J. Larsen

3M Occupational Health and Environmental Safety Division

Goals of Validation Protocols

- Define performance criteria
- Specify testing conditions and sample size to evaluate performance criteria
- Define the limitations of the sampling device

Performance Criteria

- Desorption Efficiency
- Humidity
- Sampling Rate
- Reverse Diffusion
- Storage
- Face Velocity
- Temperature and Orientation
- Relationship Between Concentration and Time

Protocol Development

- Manufacturers
- Laboratories
- NIOSH
- European Community (CEN)
- ISEA

Manufacturers

- 3M and DuPont
  - –Developed performance criteria and test conditions
- SKC developed bi-level validation technique

Laboratories

- **AIHA-Accredited Laboratories**
  - Exxon - benzene
  - Abbott - ethylene oxide
  - Goodyear - vinyl chloride
- **European Laboratories**
  - Occupational Hygiene Lab - London (1984)
  - Factorial experiments

NIOSH

- Late 1970s identified the need for a universal testing protocol
  - Specified performance criteria and experimental parameters
  - Sample size and simple statistics
- 1987 Protocol
  - Guidance document
  - Specified performance criteria
  - Sample size
  - > 200 diffusion monitors needed for a single gas and vapor analyte

CEN

- European Committee for Standardization
- Proposed Standard (prEN) "Workplace atmospheres - diffusive samplers for the determination of gases or vapors - Requirements and test methods"
- Outlines performance criteria
- Test methods specified

3M 110423

Industrial Safety Equipment Association (ISEA)

- **OSHA request for involvement in developing a protocol**
- **Safety Equipment Institute (SEI) certified**

3M Validation Protocol (Objectives)

- Outline the operating limitations
- Evaluate performance criteria
- Specify testing conditions
- Laboratories and others should be able to implement
- Results can be easily shared and understood

Desorption Efficiency
(Toluene & Methylene Chloride)

Methylene Chloride Desorption Efficiency

~ Exposure Level	Mean Mass Spiked	Mean Recovery	CV (%)
1.0 (EL)	1.59mg	0.902	5.04
0.5 (EL)	0.795mg	0.901	5.88
0.1 (EL)	0.159mg	0.877	3.63

EL: ~25ppm

Toluene Desorption Efficiency

~ Exposure Level	Mean Mass Spiked	Mean Recovery	CV (%)
1.0 (EL)	5.64mg	1.02	1.07
0.5 (EL)	3.03mg	1.02	2.57
0.1 (EL)	0.434mg	0.961	2.19

EL: ~100pm

3M 110427

Humidity

- Relationship between humidity and capacity
- Water vapor competes for active sites on carbon sorbent
- Influence of water will vary depending on chemical properties

Desorption Efficiency (Test Method)

- 3 sets of four monitors
- Vapor spike mass levels (8 hours)
  - 0.1 x EL
  - 0.5 x EL
  - 1.0 x EL
- > 75% recovery with a CV <0.1

Note: EL equals an exposure level. It may represent a TLV or PEL or other appropriate standard.

Humidity
(Toluene)

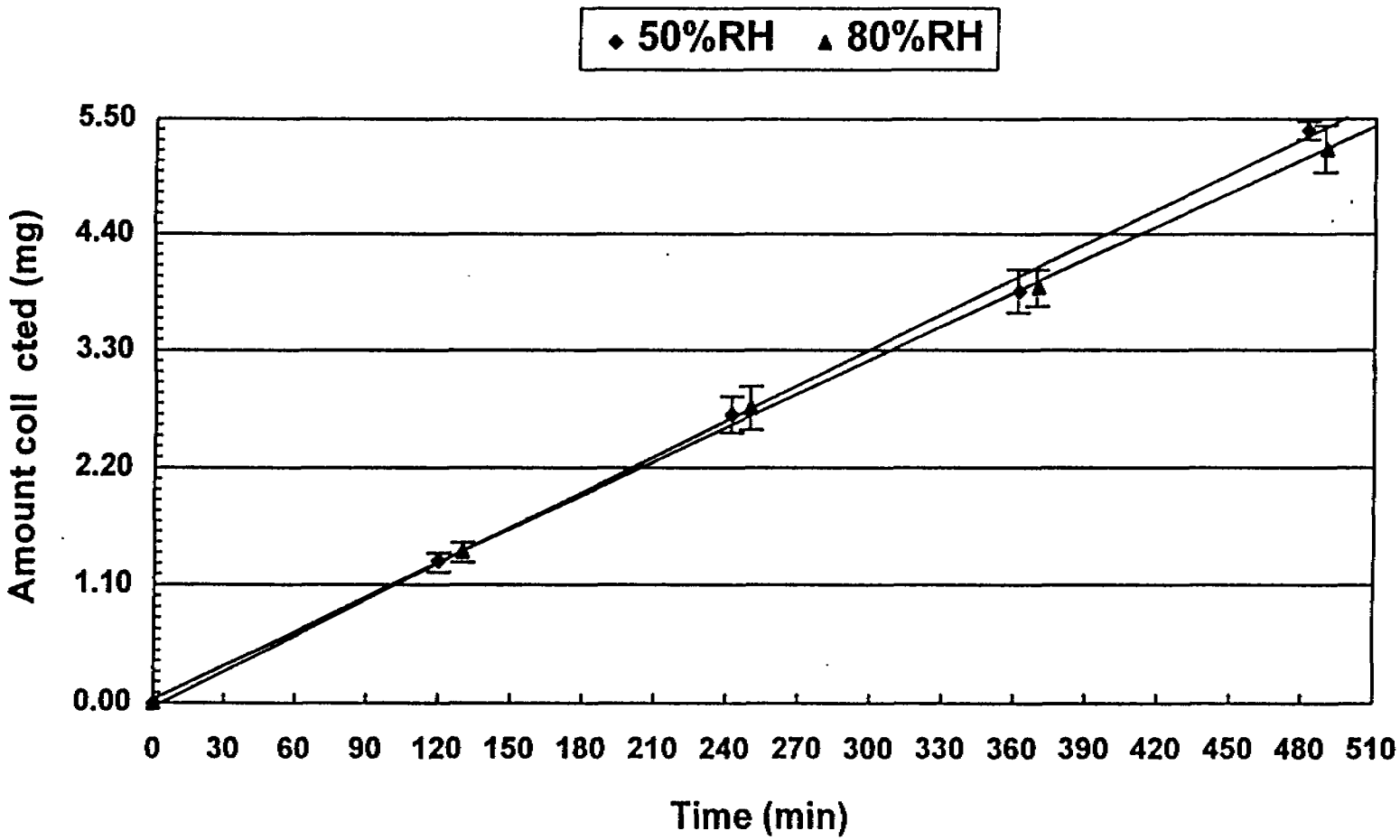
Relative Humidity (%)	2 Hour Sample (SR)	4 Hour Sample (SR)	6 Hour Sample (SR)	8 Hour Sample (SR)
50	[1] 30.8 ± 1.1	[2] 31.0 ± 1.5	[3] 29.7 ± 1.4	[4] 31.2 ± .3
80	[5] 30.4 ± 1.1	[6] 30.8 ± 2.3	[7] 29.4 ± 1.0	[8] 29.7 ± 1.4

SR = Sampling rate ± std. dev.

$\bar{x}$ SR = 30.37 ± .2 (Based on cells 1-8)

3M 110430

Toluene Humidity Effects
(1 EL, 50% & 80% RH)



Concentration vs. Time
(Toluene)

Conc/ Time	15 min. (accuracy)	240 min. (accuracy)	480 min. (accuracy)
.1 EL	1 23.8%	2	3 12.1%
1 EL	4	5	6
2 EL	11.3% 7	8	6.8% 9

EL : ~100ppm

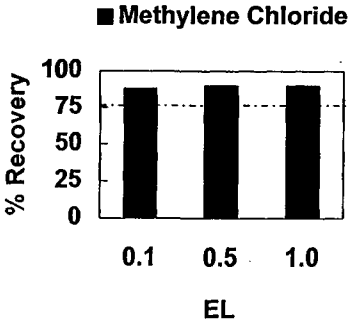
Accuracy = 2 CV ± Bias

Published SR = 31.4 cc/min.

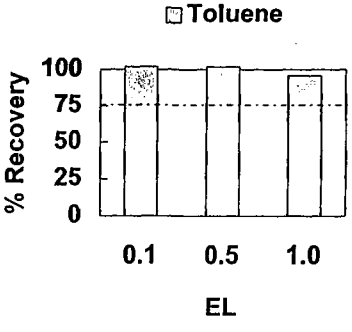
Temperature

- **Evaluate the influence of temperature on sampling rate**

Desorption Efficiency



1 EL: ~25ppm/8hrs



1 EL: 100ppm/8hrs

3M 110434

Concentration vs. Time (Methylene Chloride)

Conc/ Time	15 min. (accuracy)	240 min. (accuracy)	480 min. (accuracy)
.1 EL	1	2	3 26.6%
1 EL	4	5	6
2 EL	7 14.3%	8	9 7.7%

E L : ~25 ppm

Accuracy = 2 CV ± Bias

Published SR = 37.9 cc/min.

3M Occupational Health and
Environmental Safety Division

3M Center
St. Paul, Minnesota 55144-1000
612/733 1110

3M

December 18, 1989

Milagros Diaz Parra
Supervisor de Higiene Ocupacional
Pequiven
Apartado 159
Maracaibo,
Venezuela

FAX 011-58-66-311053/100

Dear Ms Diaz,

In response to your Fax message to Doug Taylor, here are the responses.

1. The appropriate monitor for Vinyl Chloride Monomer is the 3520. Since activated carbon has limited afinity for VCM, you should not use the 3500. I also recommend that you use the ratio of the weight of VCM analyte on the front and back sections of the 3520 as an internal check on the validity of the sample. If the amount of analyte found on the second sorbent wafer exceeds 50% of the material on the front sorbent wafer, then the sample is not valid. The details of this are covered in an 3520 Sampling Guide I am sending you.

2. I am sending you technical details of the 3720 monitor, and its validation studies in comparison to bisulfite impingers in the laboratory and field studies involving the 3720.

The temperature correction coefficient for diffusional monitors comes from theoretical treatment of diffusion processes. These apply equaly to formaldehyde difusion, and the temperature correction factors found in the sampling guide for organic vapor monitors can be used. You will note that these correction factors are not very large, and are close to the value 1.0.

The 3720 Formaldehyde Monitor can be used in a wide relative humidity range. We tested the product in RH ranges from 25% to 85%. This variation in RH has shown no variation in sampling rate.

At extremely low RH's, we expect the collection efficiency of the monitor to be affected if humidifying pad of the secondary body dries out, and the monitor sorbent cannot be humidified sufficiently during monitoring to allow the reaction of formaldehyde with the bisulfite salt in the

sorbent waf r. I would not expect this to be of concern in Venezuela.

3. Sampling Rate Validation. I am sending you a copy of the Sampling Rate validation protocol. If there are compounds you wish to monitor which do not show up in the published tables with sampling rates, please consult us. By knowing the boiling point and molecular weight of the substances, we can compute the sampling rate using the Hirshfelder Equation and communicate this to you. Although this is only a semiempirical sampling rate, it is considered accurate to within +/- 5%.

4. You will need to send the Mercury Monitor back to our Monitor Analysis service for analysis. Please send monitors to: Monitor Analysis Service
OH & ES Division
Building 76-2W-02
St Paul, MN 55107
USA

The 3600 Monitor analysis results goes back to you by 1st Class normal mail. Be sure to include your return address.

I hope this answers all your questions.

Sincerely,

Paul E Olson
International Technical Manager
3M/Occupational Health and Environmental Safety Division

cc: Doug Taylor - 220 - 3E - 04
Antonio Mata - 3M Venezuela

Internal Correspond nce

dc P.F.Guehler

To: E. D. HORNE

From: L. W. ANDERS

Subject: NIOSH RECOMMENDATION

Date: January 6, 1982

3M

The attached NIOSH letter of October 9, 1979 is the only written recommendation: In the second paragraph, "NIOSH's immediate recommendation will be to encourage use of the OVM #3500 for those compounds which have a complete set of data to verify among other properties, the capacity, recovery coefficient, and upper exposure limit at high humidity of the badge for the compound. These data may come from a variety of sources which include your laboratories as well as ours .... As new compounds qualify, the use of the monitor will be expanded".

We have done an extensive amount of documentation of sampling rate, capacity, recovery coefficient and upper exposure limits. This information was used to publish the new Sampling and Analysis Guide in May 1981. The technical documentation from the attached list of publications has all been summarized in the above Guides for easy reference. The accuracy and precision of the sampling rate is documented in publications 7, 9 and 11. The capacity for various organic contaminants is documented in publications 5, 10, 12, and 13. The determination of recovery coefficient is documented in publication 2. The upper exposure limit at high relative humidity in publication 5, 6, 10, and 12.

The above information provides a complete set of data for every compound in the new Sampling and Analysis Guides and therefore fulfills the NIOSH requirements to give immediate recommendation for encouraged use of the OVM #3500.

LWA

L. W. Anders/ss
Attachments

1. A NEW PERSONAL ORGANIC VAPOR MONITOR WITH IN-SITU SAMPLE ELUTION, D.W.Gosselink, D.L.Braun, H.E.Mullins, and S.T. Rodriguez, Occupational Health & Safety Products Division, 3M Company, St. Paul, Minnesota 55144

   AIHA Conference, Los Angeles, May 1978 Submitted for publication

2. DETERMINATION OF DESORPTION EFFICIENCIES IN THE 3M 3500 ORGANIC VAPOR MONITOR, S.T.Rodriguez, D.W.Gosselink, and H.E.Mullins, Occupational Health & Safety Products Division, 3M Company, St. Paul, Minnesota 55144

   AIHA Conference, Houston, May 1980

3. DIFFUSIONAL SAMPLING PRINCIPLES, THEORIES AND INDUSTRIAL APPLICATIONS, L.W.Anders, Occupational Health & Safety Products Division, 3M Company, St. Paul, Minnesota 55144

   AIHA Conference, Houston, May 1980 and Portland, May 1981

4. DIFFUSIONAL MONITORING: A NEW APPROACH TO PERSONAL SAMPLING, D.W.Gosselink, D.L.Braun, H.E.Mullins, S.T.Rodriguez, and F.W.Snowden, Chemical Hazards in the Workplace, Measurement, and Control, G. Choudbary, Ed. ACS Symposium Series 149, 1981

5. TECHNIQUE FOR DETERMINING CAPACITY OF DIFFUSIONAL SAMPLING DEVICES, L.W.Anders, Occupational Health & Safety Products Division, 3M Company, St. Paul, Minnesota 55144

   AIHA Conference, Portland, May 1981 To be submitted for publication

6. COMPARISON OF DIFFUSIONAL ORGANIC VAPOR MONITORS WITH CHARCOAL TUBES FOR SAMPLING LABORATORY CHALLENGES TO CONTAMINANT MIXTURE, L.W.Anders and H.E.Mullins, Occupational Health & Safety Products Division, 3M Company, St. Paul, Minnesota 55144

   AIHA Conference, Portland, May 1981
   To be submitted for publication

7. DOCUMENTATION OF SAMPLING RATES FOR THE 3M ORGANIC VAPOR MONITOR, L.W.Anders, Occupational Health & Safety Products Division, 3M Company, St. Paul, Minnesota 55144

   ASTM Symposium,Boulder, August 1981

   DIFFUSIONAL SAMPLING PRINCIPLES, THEORIES AND APPLICATION TO SAMPLING AMBIENT ATMOSPHERES FOR ENVIRONMENTAL CONTAMINANTS, L.W.Anders and R.M.Shor, Occupational Health & Safety Products Division, 3M Company, St. Paul, Minnesota 55144

   EPA Symposium, Raleigh, May 1982
   To be submitted for publication

9. DOCUMENTATION OF SAMPLING RATE ACCURACY AND PRECISION FOR DIFFUSIONAL DEVICES USED FOR PERSONAL AND ENVIRONMENTAL SAMPLING, L.W.Anders, R.M.Shor, and H.E.Mullins, Occupational Health & Safety Products Division, 3M Company, St. Paul, Minnesota 55144

EPA Symposium, Raleigh, May 1982
To be submitted for publication

10. DIFFUSIONAL SAMPLING OF CHLORINATED ORGANIC CONTAMINANTS FROM KNOWN LABORATORY CHALLENGES, L.W.Anders and R.M.Shor, Occupational Health & Safety Products Division, 3M Company, St. Paul, Minnesota 55144

EPA Symposium, Raleigh, May 1982
To be submitted for publication

11. SAMPLING RATE VALIDATION PROTOCOL FOR ORGANIC VAPOR DIFFUSIONAL SAMPLERS, L.W.Anders and H.E.Mullins, Occupational Health & Safety Products Division, 3M Company, St. Paul, Minnesota 55144

AIHA Conference, Cincinnati, June 1982
To be submitted for publication

12. DIFFUSIONAL SAMPLING DEVICE PERFORMANCE WITH HIGHLY VOLATILE COMPOUNDS, R.M.Shor and L.W.Anders, Occupational Health & Safety Products Division, 3M Company, St. Paul, Minnesota 55144

AIHA Conference, Cincinnati, June 1982
To be submitted for publication

13. A DIFFUSIONAL ORGANIC VAPOR MONITOR WITH A SECONDARY ADSORBENT FOR MEASURING OVERLOAD WITH EXTENSION OF TOTAL SAMPLING CAPACITY, L.W.Anders, P.L.Sullivan, and H.E.Mullins, Occupational Health & Safety Products Division, 3M Company, St. Paul, Minnesota 55144

AIHA Conference, Cincinnati, June 1982
To be submitted for publication

14. SAMPLING RATE EVALUATION OF DIFFUSIONAL SAMPLERS AS A FUNCTION OF PATH LENGTH WITH TRANSIENT CHALLENGE CONCENTRATION, L.W.Anders and R.M.Shor, Occupational Health & Safety Products Division, 3M Company, St. Paul, Minnesota 55144

AIHA Conference, Cincinnati, June 1982
To be submitted for production

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
CENTER FOR DISEASE CONTROL

NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
ROBERT A. TAFT LABORATORIES
4676 COLUMBIA PARKWAY, CINCINNATI, OHIO 45226

RECEIVED
OCT
E. D. HORNE

October 9, 1979

Mr. Einar D. Horne
Technical Director
Occupational Health & Safety
Products Division/3M
230-B 3M Center
Saint Paul, Minnesota 55101

Dear Einar:

On behalf of John Crable, Larry Doemeny, Chuck Geraci, Mary Lynn Woebkenberg and myself, I want to thank you and your co-workers for taking the time to meet with us on September 25. We found the exchange of information quite useful, as I hope you did. Because of our meeting, we are able to liberalize our recommendation on NIOSH's use of the Organic Vapor Monitor #3500.

Due to the discrepancy over methylene chloride, our immediate recommendation will be to encourage use of the OVM #3500 for those compounds which have a complete set of data to verify, among other properties, the capacity, recovery coefficient and the upper exposure limit at high humidity of the badge for the compound. These data may come from a variety of sources which include your laboratories as well as ours. In general, my recommendation will involve increased usage for compounds with moderate to low vapor pressures and moderate to low TLV's. Conversely, I will continue to take a conservative approach with high vapor pressure, high standard compounds. As new compounds qualify, the use of the monitor will be expanded. For this reason, I am asking you to send qualification information to Dr. Charles Geraci and Ms. Mary Lynn Woebkenberg as it becomes available.

Pl ase keep in touch on this matter, as together we can do a great deal to promote the use of accurate and precise diffusion monitors in field industrial hygiene.

Sincerely yours,

Walter M. Haag

Walter M. Haag
Director, Division of Physical
Sciences and Engineering

TECH DATA BULLETIN

TECHNICAL BULLETIN

ANOTHER STEP TOWARDS BETTER OCCUPATIONAL HEALTH AND SAFETY

3M Analytical Service does not analyze samples of compounds not appearing on the Compound Guide. This policy may not have been clear in the past, therefore, as of January 1, 1980 only compounds appearing on the NEW Compound Guide will be analyzed by 3M.

3M Analytical Service, through Tech Service, will continue to provide information, such as sampling rates or methods of calculating sampling rates for compounds not on the New Compounds Guide, but for which the OVM 3500 can be used. The list of compounds on the New Compound Guide will be updated if new compounds are added.

The following list of compounds is taken from the NEW Compound Guide. It is not an exhaustive list of compounds for which the OVM can be used, but it lists the only compounds that will be analyzed by 3M Analytical Service.

Occupational Health & Safety Products Division 3M COMPANY
3M CENTER · SAINT PAUL, MINNESOTA 55101

COMPOUNDS ANALYZED BY 3M ANALYTICAL SERVICE

Acetone

Acetonitrile

Acrylonitrile

Allyl Alcohol

Allyl Chloride

Amyl Acetate

sec-Amyl Acetate

iso-Amyl Alcohol

sec-Amyl Alcohol

Benzene

Benzyl Chloride

Bromoform

Butadiene

Butyl Acetate

iso-Butyl Acetate

sec-Butyl Acetate

tert-Butyl Acetate

Butyl Alcohol

iso-Butyl Alcohol

sec-Butyl Alcohol

tert-Butyl Alcohol

Butyl Cellosolve

p-tert-Butyl Toluene

Camphor

Carbon Tetrachloride

Cellosolve

Cellosolve Acetate

Chlorobenzene

Chlorobromomethane

Chloroform

1-Chloro-1-Nitropropane

Cumene

Cyclohexane

Cyclohexanol

Cyclohexanone

Cyclohexene

Diacetone Alcohol

Dibutyl Phthalate

O-Dichlorobenzene

P-Dichlorobenzene

Diethyl Phthalate

Diisobutyl Ketone (DiBK)

Dimethyl Formamide (DMF)

Dioxane

Enflurane (2-Chloro-1,2-trifluorethyl difluoromethyl ether)

Epichlorohydrin

Ethyl Acetate

Ethyl Acrylate

Ethyl Benzene

Ethyl Bromide

Ethyl Ether

Ethylene Chlorohydrin

Ethylene Dibromide

Ethylene Dichloride (1,2-Dichloroethane)

Freon 11: Fluorotrichloromethane

Freon 12: Dichlorodifluoromethane

Freon 13: Chlorotrifluoromethane

Freon 14: Tetrafluoromethane

Freon 21: Dichloromonofluoromethane

Freon 22: Chlorodifluoromethane

Freon 23: Trifluoromethane

Freon 112: 1,1,2,2-Tetrachloro 1,2-Difluoroethane

Freon 113: 1,1,2-Trichloro-1,1,2-Trifluoroethane

Freon 114: 1,2-Dichloro 1,1 2,2-Tetrafluoroethane

Freon 115: 1-Chloro-1,1, 2,2,2-Pentafluoroethane

Freon 116: Perfluoroethane

Freon 12B2: Dibromodifluoromethane

Freon 13B1: Trichloromonobromomethane

Furfural

COMPOUNDS ANALYZED BY 3M ANALYTICAL SERVICE (CONT'D)

Glycidol

Heptane

Hexane

Halothane (2-bromo-2-Chloro-1,1,1-Trifluoroethane)

Isophorone

Mesityl Oxide

Mesitylene

Methyl Acetate

Methyl Acrylate

Methyl Butyl Ketone (MBK)

Methyl Cellosolve

Methyl Cellosolve Acetate

Methyl Chloroform (1,1,1-Trichloroethane)

Methyl Ethyl Ketone (MEK)

Methyl Isobutyl Ketone (MIBK)

Methyl Propyl Ketone

Naphthalene

Nitrobenzene

n-Octane

Pentane

Perchloroethylene (Tetrachlorethylene)

Phenyl Ether

Propyl Acetate

Isopropyl Acetate

Propyl Alcohol

Isopropyl Alcohol

Isopropyl Ether

Propylene Dichloride

Stoddard Solvent

Styrene

1,1,2,2-Tetrachloroethane

Toluene

1,1,2-Trichloroethane

Trichlorethylene

Vinyl Chloride

Vinyl Toluene

Xylene

TECH DATA BULLETIN

3M

Number: 63

Product: 3M Organic Vapor Monitor #3520

Subject: Sampling For Butadiene

I. INTRODUCTION

This technical data bulletin contains information to be used when sampling atmospheres for butadiene using the 3M Organic Vapor Monitor with back-up section #3520.

Because of the low capacity of the charcoal sorbent for butadiene, use of the single sorbent Organic Vapor Monitor #3500 is not recommended.

II. SAMPLING RATE

5.67 ug/ppm-hr

42.8 cc/min

III. CAPACITY

The capacity of the charcoal sorbent for butadiene is highly dependent upon the relative humidity during the sampling period. The capacity of a single carbon wafer is:

Relative humidity greater than 60% :	40 micrograms
Relative humidity 60% or less:	290 micrograms

IV. MINIMUM DETECTABLE LEVEL

The minimum reliable quantitative level is 4.0 micrograms.

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St. Paul, Minnesota 55144-1000

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V. RECOMMENDED SAMPLING TIMES

Recommended sampling time is shown as a function of the ambient concentration of butadiene and the relative humidity during the exposure period in figures one through three.

The minimum sampling time is defined as the time required to collect 4.0 micrograms, the minimum reliable quantitation level.

Although at concentrations above 3 ppm the sampling time required to reach 4 micrograms is less than 15 minutes, a 15 minute sampling time is the minimum recommended. This minimizes the errors inherent in short term sampling.

The maximum sampling time is defined as the time required to exceed the capacity of the monitor. The capacity of the #3520 Organic Vapor Monitor is approximately three times that of the Single Wafer Monitor #3500. All sampling times are calculated for the #3520 monitor.

A. Relative Humidty Greater Than 60%

At an ambient relative humidity greater than 60%, the sampling time is shown as a function of butadiene concentration up to 10 ppm in figure one. At any given concentration, a sampling time in the shaded area of the graph will be within the operating limits of the monitor.

At concentrations above 10 ppm (figure two) the maximum sampling time intersects the 15 minute recommended minimum at 85 ppm. Due to the small difference between minimum and maximum sampling time at higher concentrations, sampling above 50 ppm is not recommended.

B. Relative Humidity of 60% or less

The capacity of the Organic Vapor Monitor is greatly expanded at relative humidities of 60% or less. This is shown in figure three.

At concentrations of less than 1 ppm, the minimum sampling time is the same as given in figure one. The maximum sampling time exceeds 100 hours.

C. Illustrative Example

To determine sampling times, measure the relative humdity and estimate a possible range of concentrations based upon previous sampling data.

The lowest concentration will determine the minimum sampling time and the highest concentration will determine the maximum sampling time.

For example, consider an exposure at 85% RH with an estimated concentration between 1 and 10 ppm. Using figure one, at one ppm the minimum sampling time is 0.75 hours. The maximum sampling time at 10 ppm is 3 hours. Thus, any exposure time between 45 minutes and 3 hours would be within the limits of the monitor for concentrations between 1 and 10 ppm at 85% RH.

If there is no previous sampling data, it is suggested that sampling be conducted for 2, 4 and 6 hours.

VI. ANALYTICAL PARAMETERS

A. Desorbing Solvent: Methylene Chloride

B. Recovery Coefficient: It is recommended that the analyst run a "working curve" for each batch of analysis. Typical values would be 0.8 - 0.9.

VII. MONITORING FOR BUTADIENE AND ACRYLONITRILE

Butadiene and acrylonitrile can be collected on the same monitor. The capacity of the monitor for acrylonitrile is not a limiting factor. The sampling parameters should be determined by butadiene.

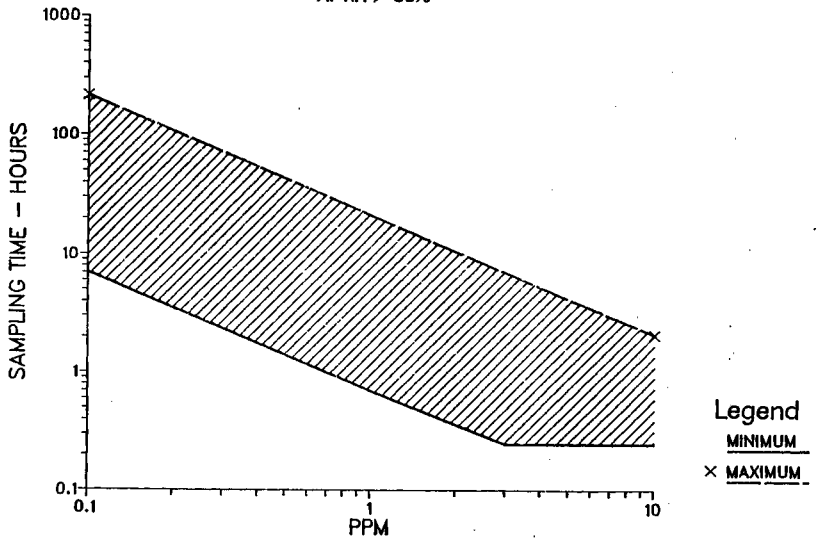
Both butadiene and acrylonitrile can be desorbed with methylene chloride.

VIII. MONITORING BUTADIENE, ACRYLONITRILE, AND STYRENE

Use of the #3520 to sample for butadiene, acrylonitrile, and styrene simultaneously is not recommended due to the low recovery of styrene when desorbed wth methylene chloride.

When sampling for these three compounds, it is recommended that the butadiene and acrylonitrile be collected on one #3520 Monitor and desorbed with methylene chloride, and the styrene be collected on a separate #3500 OVM and desorbed with carbon disulfide.

FIGURE ONE
RECOMMENDED SAMPLING TIME
BUTADIENE COLLECTED ON #3520
AT RH > 60%



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3M 105173

FIGURE TWO
RECOMMENDED SAMPLING TIME
BUTADIENE COLLECTED ON #3520
AT RH > 60%

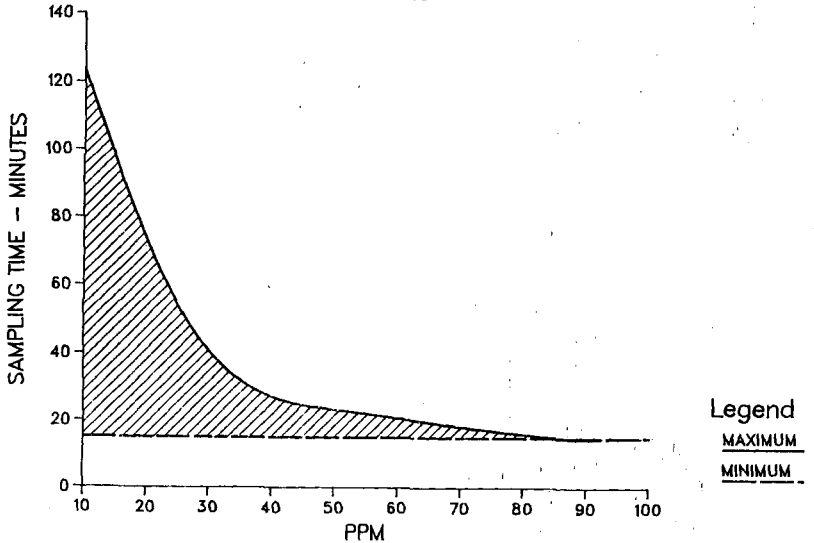

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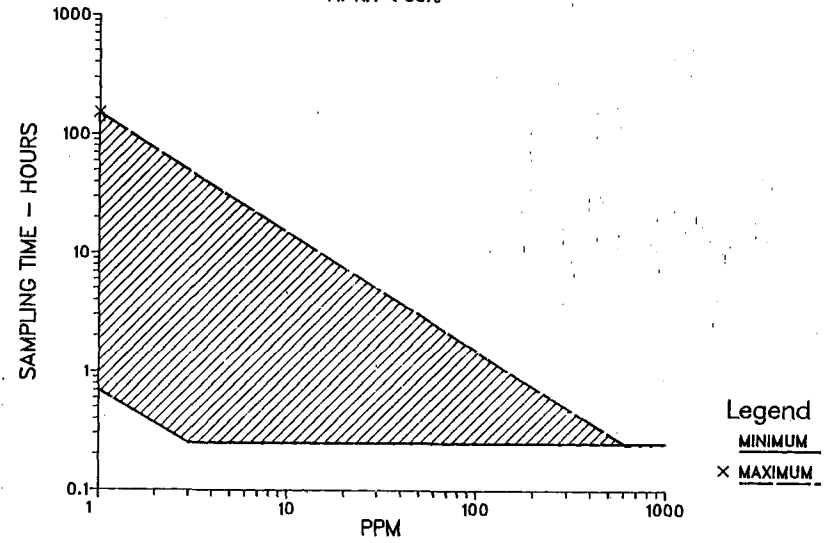
FIGURE THREE
RECOMMENDED SAMPLING TIME
BUTADIENE COLLECTED ON #3520
AT RH < 60%



BUT9 .DAT JAK 1/86

3M 105175

TECH DATA BULLETIN

3M

Number: 71

Product: 3M ORGANIC VAPOR MONITORS

Subject: SAMPLING FOR METHYLENE CHLORIDE

I. INTRODUCTION.

Active carbon has been shown to have a poor affinity for methylene chloride. This has resulted in strict limitations upon sampling times when using the 3M organic vapor monitors for sampling this compound.

Recent experimental data suggests that an organic vapor monitor will sample methylene chloride satisfactorily when used within the sampling time guidelines and under steady state conditions. However, when the monitor is used in nonsteady state conditions, with varying concentrations of methylene chloride in the atmosphere, it is possible to get desorption and subsequent sample loss when the ambient concentration of methylene chloride becomes zero. This sample loss could result in a sampling error, with the reported concentration less than the true ambient concentration.

II. SAMPLING RECOMMENDATIONS.

Use of the 3M Organic Vapor Monitor #3500 is not recommended for methylene chloride.

Only the #3520 Organic Vapor Monitor with back-up section should be used for sampling methylene chloride.

III. SAMPLING GUIDELINES.

Maximum Sampling Time: 4 hours

Max. Qty. of Methylene Chloride on Top Wafer: 2000 micrograms

If the quantity of methylene chloride on the back-up wafer exceeds 50% of the amount on the top wafer, the sample is invalid. If this occurs, the sampling should be repeated using a shorter sampling period.

IV. ACCURACY.

The capacity of the carbon wafers in the #3520 Organic Vapor Monitor for methylene chloride is strongly influenced by the presence of water vapor and competing organic vapors. This introduces an uncertainty into the results of analysis for methylene chloride.

The accuracy of the #3520 Organic Vapor Monitor when used to sample methylene chloride can be as low as ± 50% if high humidity or competing organic vapors are present.

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TECH DATA BULLETIN

3M

Number: 70

Product: #3510 Organic Vapor Monitor

Subject: Compound Selection List Changes

Listed below are 14 compounds which have been eliminated from the #3510 Organic Vapor Monitor (with prepaid analysis) selection list. A recommended sampling procedure is listed.

COMPOUND	RECOMMENDED SAMPLING PROCEDURE	#3520 MAXIMUM SAMPLING TIME AT PEL (HOURS)	
		RH < 70%	RH > 70%
ACETONE	#3520 OVM	2	2
ACETONITRILE	#3520 OVM	8	4
ALLYL CHLORIDE	#3520 OVM	8	8
CHLOROBROMOMETHANE	See Tech Data Bulletin #71		
DIMETHYL FORMAMIDE	Solid Sorbent Tube (Silica Gel, 150 mg/75 mg)		
DICHLOROMETHANE (Methylene Chloride)	See Tech Data Bulletin #71		
ETHYL BROMIDE	Solid Sorbent Tube (Coconut Shell Charcoal 100 mg/50 mg)		
ETHYL ETHER	Solid Sorbent Tube (Coconut Shell Charcoal 100 mg/50 mg)		
ETHYELNE DIBROMIDE	#3500 OVM - Analyzed by ECD Gas Chromotography		
FREON 113 (1,1,2-Trichloro, 1,2,2-Trifluoroethane)	NIOSH Method #S129 2nd Edition, Vol. 2		

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METHYL ACETATE	#3520 OVM	2	2
PENTAINE	#3520 OVM	1.5	1.5
ISOPROPYL ETHER	#3520 OVM	3	3
1,1,1-TRICHLOROETHANE (Methyl Chloroform)	#3520 OVM	4	4

For additional information, please contact OH&SP Technical Service at 1-800-243-4630.

Operationally, passive dosimeters are ideally suited for monitoring organic vapors in hospital operating rooms as they are compact, lightweight and do not require tubing or pumps. In this study, a recently developed passive diffusion sampler was used to collect 2-bromo-2-chloro-1,1,1-trifluoroethane (Halothane) and 2-chloro-1,1,2-trifluoroethyl difluoromethyl ether (Enfluran®) in standard air mixtures over the range of 0.2 - 10 ppm. Additionally, exposures to known concentrations were conducted for various lengths of time. A side-by-side comparison of charcoal tubes (CT) and passive dosimeter collection characteristics were made on known air mixtures and samples collected in operating rooms. The material adsorbed on charcoal from dosimeters and CT was desorbed with carbon disulfide and quantified using gas-liquid chromatography. The overall efficiency of the dosimeters along with quality control data are presented.

Evaluation of a passive dosimeter for collection of 2-bromo-2-chloro-1,1,1-trifluoroethane and 2-chloro-1,1,2-trifluoroethyl difluoromethyl ether in hospital operating rooms

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US Army Environmental Hygiene Agency, Aberdeen Proving Ground, MD 21010

introduction

It was almost a hundred years after the first use of an inhalation anesthetic in 1842 before anesthesiologists recognized the possible deleterious effects of occupational exposure to anesthetic gases. However, it has only been during the past decade that considerable effort has been directed toward the determination of trace concentrations of anesthetic gases and vapors in the operating room atmosphere, and the related potential hazards to chronically exposed personnel.

In 1974, the American Society of Anesthesiologists Ad Hoc Committee on the Effects of Trace Anesthetics published a report on a national survey conducted on occupationally related diseases among dental and operating room personnel.[1,2] At the time of this study, the number of operating room, dental, and veterinary personnel who were potentially exposed to anesthetic gases exceeded 200 000 persons per year. The results of this study, and others both human and animal, suggest that chronic exposure to anesthetic gases increases the risk of spontaneous abortion and congenital abnormalities in children of both female workers and wives of male workers. Chronically exposed personnel also showed increased incidence of hepatic and renal diseases. Other studies have indicated an increased risk of cancer and possible impairment of certain psychologic functions. Acute exposures to anesthetic gases have been shown to affect the central nervous system with resulting symptoms of headaches, nausea, fatigue, etc.[3]

For reasons of both efficacy and safety, most of the anesthetic agents introduced prior to 1950 have been replaced. The flammable and explosive inhalation anesthetic agents such as diethyl ether and cyclopropane have been replaced by nonexplosive, nonflammable anesthetics such as halothane, enflurane, and methoxyflurane. Halothane and enflurane are currently the two most widely used halogenated anesthetic agents in US Army hospitals. They are generally used in conjunction with nitrous oxide and/or intravenously injected anesthetics.

The US Army Environmental Hygiene Agency (USAEHA) is responsible for monitoring potential problem areas of occupational hazards and safety in US Army hospitals and clinics. Part of this surveillance program is concerned with operating room engineering controls and work practices affecting personnel exposure to waste anesthetic gases. Waste inhalation anesthetic gases are those gases and volatile liquids which are inadvertently released into work areas either by faulty equipment or improper work practices. Scavenging systems designed to collect waste anesthetic gases and vapors from the breathing system at the point of discharge and disposing of them outside of the operating room are the primary means of controlling waste anesthetic gases. Sufficient ventilation rates within the operating room are necessary to dilute anesthetic agents that are not captured by the scavenging system. Failure to control properly one or more of the above-mentioned sources of waste anesthetic gases can result in potentially hazardous exposures to operating room personnel. Consequently, personal and general area monitoring of operating rooms are conducted by USAEHA to determine if a health hazard exists and to pinpoint sources of exposure, whether they be defective equipment, inadequate scavenging systems, poor ventilation, or improper administration of anesthetics. After identifying the cause

The opinions or assertions contained herein are the private views of the authors and are not to be construed as reflecting the views of the Department of the Army or the Department of Defense.

and extent of exposure, recommendations are made for improving work practices and engineering controls to meet the recommended levels for occupational exposure published by the National Institute for Occupational Safety and Health (NIOSH).

At present, a safe level of exposure for waste anesthetic gas has not been established by NIOSH; instead, it recommends that exposures be suppressed to the greatest extent possible to minimize risk to operating room personnel. When used alone, NIOSH recommends occupational exposure to halothane and enflurane be controlled so that no worker is exposed at concentrations greater than 2 ppm. For halothane and enflurane their weights corresponding to 2 ppm would be 16.15 mg/cu m and 15.10 mg/cu m, respectively. These concentrations are based on a 45-liter charcoal tube sample taken over a time period not exceeding 1 hour. When halogenated agents are used in combination with nitrous oxide, levels of approximately 0.5 ppm are achievable, provided the time weighted average of nitrous oxide is controlled at the recommended 25 ppm level.

The NIOSH criteria document, "Occupational Exposure to Waste Anesthetic Gases and Vapors,"[3] provides a comprehensive review of sampling methods, analytical procedures, and real-time monitors. Typical collection methods cited in the literature include those utilizing gas syringes,[4-7] plastic sample bags,[8] and charcoal tubes.[9] These procedures make use of gas chromatography (GC) for the analysis of isolated samples. Additional analytical methods for anesthetic gases[10-15] based on GC, infrared troscopy (IR), and gas chromatography and mass trometry (GC-MS) have also been described in the literature. The forenoted procedures have proved adequate for in-depth investigations and have been used extensively in research studies. For the purpose of routine personal monitoring however, these procedures have certain shortcomings. Some of the problems relate to equipment complexity, sample collection, and sample manipulation.

Because of the unique working conditions that exist in operating rooms, it is essential that a personal sampler for monitoring worker occupational exposure meet certain performance criteria. Foremost, the collection of samples must not interfere with any of the various tasks performed by operating room personnel. In addition, areas designated as sterile zones must not be contaminated. Finally, the air sample should be proportional to a time-weighted average of anesthetic agent concentration.

Traditionally, organic vapors have been collected and concentrated using the charcoal tube (CT) technique. This method consists of pumping a known volume of air through a tube packed with charcoal for a definite period of time. Organic vap rs are adsorbed onto the charcoal and subsequently desorbed with an appropriate solvent. The desorbent is analyzed with a gas chromatograph.

An alternative approach to sampling organic vapors is through consideration of fundamental molecular diffusion metry. Devices based on this principle have recently found their way into the industrial hygiene marketplace, and have been used selectively for the collection of certain organic vapors. With this type of sampler, volatile compounds enter the sampler by molecular diffusion such that the rate of sample collection is a function of the organic vapor concentration in air. Since the vapors enter the dosimeter by nonmechanical means, it requires neither calibration nor electrical power.

The purpose of this investigation was to determine the suitability of the 3M Organic Vapor Monitor (OVM) for the collection of halothane and enflurane in operating room environments. Side-by-side collection of known concentrations of halothane and enflurane were conducted with OVM and CT samplers for comparison and correlation of test data. Variables studied were sampling time, sample concentration, and storage stability. In addition to the laboratory tests, samples were collected in operating rooms during administration of anesthesia to patients undergoing surgery. The effects of humidity and temperature on collection efficiency were not included in this study, since these parameters are carefully regulated in operating rooms.

experimental

passive dosimeter

All passive dosimeter monitoring was conducted with the 3M Brand Model 3500 Organic Vapor Monitor (OVM), 3M Company, St. Paul, MN. This unit consists of a round nylon body approximately 4.5 cm in diameter, weighing about 12 grams. A charcoal adsorbent pad is located inside the monitor, separated by spacers from a diffusion membrane. Contaminants enter the monitor by molecular diffusion and are adsorbed onto the charcoal. At the conclusion of the sampling period, the diffusion membrane is removed, and a tight-fitting cap firmly snapped into place. The cap contains two ports which are sealed by inserting the attached plugs. When the sample is ready for chromatographic analysis, the center port is opened and 1.5 mL of carbon disulfide is introduced into the monitor via a glass syringe. The center port is resealed, and the sample is allowed to desorb for 30 minutes. A GC sample is taken directly from the center port with a 10-μL syringe. The OVM sampler and cover are shown in Figure 1.

The time-weighted worker exposure level is calculated using the following equations:

$$\text{mg/m}^3 = \frac{\text{Corrected weight on badge (nanograms)}}{\text{Sampling rate (cm}^3\text{/min)} \times \text{Sampling time (min)}}$$

$$\text{ppm} = \frac{\text{mg}}{\text{m}^3} \times \frac{22.4\ \text{L/mole}}{\text{mwg/mole}} \times \frac{T^\circ\text{K}}{273^\circ\text{K}} \times \frac{760\text{-mm Hg}}{\text{P-mm Hg}}$$

The sampling rates for halothane and enflurane are 25.1 cm^3/min and 26.9 cm^3/min, respectively. These sampling rates were calculated from diffusion coefficients corresponding to each compound.

charcoal tube monitor

Charcoal tubes containing two sections of charcoal, 200/400 mg, were purchased from SKC Inc., Eighty Four, PA. Samples were collected at two different sampling rates, 30 mL/min (Accuhaler 808, Lefco Engineering) and 500

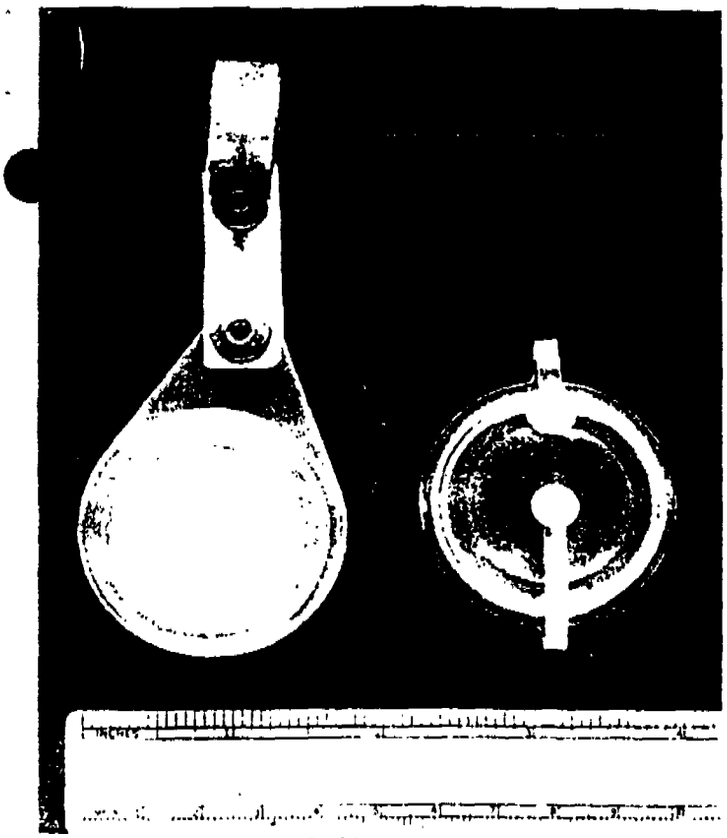

Figure 1 – OVM sampler and cover.

mL/min (Model P-4000A, E. I. du Pont de Nemours & Co., Wilmington, DE). Pump calibration was accomplished by connecting a charcoal tube to a pump and measuring the air flow with a bubble meter. When the sample was ready for chromatographic analysis, the charcoal was poured from the glass sampling tube into a 10-mL vial and desorbed with 2 mL of carbon disulfide.

gas chromatography

Analysis of desorbent solutions was performed on a Hewlett-Packard Model 5830 gas chromatograph equipped with a flame ionization detector and HP 18850A GC Terminal. The GC operating conditions were as follows: column, 17 ft. × 1/8 in. stainless steel packed with 30% Apeizon L on 80-100 mesh Chromosorb W-HP; injection port temperature, 130° C; detector temperature, 300° C; initial column temperature, 120° C; final column temperature, 190° C; column temperature programming rate, 30°/min.

test atmosphere

Appropriate amounts of halothane and enflurane were injected into a 2-mL vial equipped with a septum and screw cap. The vial was transferred to a 6920-liter static test chamber and positioned in front of a circulating fan. The vial cap was removed and the chamber door closed immediately. After sealing the door, the circulating fan was turned on and 30 minutes were allowed to elapse to insure complete mixing of the anesthetic agents with air. The OVM's were attached to a meter stick and inserted into the chamber through a side-access port. CT samples were collected at a port adjacent to the OVM's. For some experiments having short sample collection times, successive tests were conducted using the same chamber concentration.

results and discussion

OVM and CT data for various concentrations of halothane and enflurane are presented in Table I. Test atmospheres for Samples 1-3 contained only halothane, whereas test Samples 4-8 were binary mixtures of both halothane and enflurane. The sampling rate for Samples 6 and 7 was 30 mL/min; the sampling rate for all other samples was 500 mL/min. In general, results from the OVM's were in good agreement with the theoretical values; whereas, results from the CT's showed a slight positive bias. Statistical treatment of the OVM data is presented in Table II.

The values shown in Table II were derived from four replicates for each test. Since the GC analysis is an integral part of each test, the statistical data reflect the overall efficiency of both sample collection and analytical procedures. In general, the precision and accuracy were within acceptable limits over the tested concentration range. In summary, a total of 44 OVM's were tested for halothane, and 25 OVM's for enflurane, at four concentration levels (0.5, 2, 5, and 10 ppm). An overall recovery of 100.6% and a

TABLE I
Halothane and Enflurane Laboratory Data

Sample	Exposure Time OVM, Hrs	Theoretical Conc., ppm	Mean Observed Enflurane, ppm OVM[A]	Mean Observed Enflurane, ppm CT[B]	Mean Observed Halothane, ppm OVM[A]	Mean Observed Halothane, ppm CT[B]
1	4	5	--	--	5.28	5.14
2	2	5	--	--	5.34	5.40
3	4	2	--	--	2.13	2.23
4	4	0.5	0.57	0.64	0.48	0.59
5	4	2	1.95	2.13	2.27	2.30
6	2	2	1.65	2.47	2.06	2.22
7	1	2	2.01	2.11	1.95	2.11
8	4	10	9.17	11.49	9.51	10.30

[A]Average of four OVM's.

[B]Average of two CT's for Samples 6 and 7; all others average of four CT's.

TABLE IV
Field Data

Sample	Halothane OVM ppm[A]	Halothane CT ppm[B]	Halothane IR ppm[C]	Enflurane OVM ppm[A]	Enflurane CT ppm[B]
1	3.42	3.43	3.53	--	--
2	1.87	2.04	1.78	--	--
3	0.40	0.56	0.55	--	--
4	--	--	--	0.49	0.52
5	--	--	--	1.39	(N)
6	--	--	--	0.58	(N)

[A]Average of four OVM's.

[B]Average of two CT's.

[C]Integration of chart reading.

(N)Not taken so as to not interfere with operating room procedures.

dosimeters come preassembled, whereas CT dosimeters require on-site assembly of components. Most important, utilization of the OVM does not interfere with personnel work routines nor present a contamination problem. Finally, the OVM becomes cost-effective when one takes into account equipment costs and personnel time required for the operation and maintenance of a charcoal tube sampling system.

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AWS Safety/Health research program fund drive

The American Welding Society has launched a major fund drive to support a Welding Safety and Health Research Program with the overall objectives of: 1) demonstrating that the welding environment can be safe when responsible environmental precautions are followed and 2) meeting government requirements, that are technically and economically feasible.

One long range research project will be concerned with the health effects of the welding environment on those who work with mild steel. Other research projects that are planned include a detailed chemical analysis of welding fume, a design for optimum ventilation systems, and short and long-term animal testing to predict health effects. Safety training materials will be developed as part of this Research Program.

All companies and organizations within the welding industry, as well as all those with a vested concern for advancements in the fields of occupational safety and health, are being asked to financially support this Research Program to a reasonable degree — consistent with the importance of welding within the individual company or organization structure.

To fund the projects now ready for implementation, a minimum of $500,000 is required per year for the next five to ten years.

A brochure "Creating a Healthful Environment . . . a Challenge to the Welding Industry" containing additional details on this Program, is available from Publications Services, American Welding Society, 2501 N.W. 7th Street, Miami, FL 33125. Telephone 305/642-7090. For additional information on this Program, contact Marvin Kennebeck, AWS Safety and Health Manager, at the American Welding Society.

3M BRAND ORGANIC VAPOR MONITOR
PRODUCT NO. 3500

Qualification Data for *Carbon Tetrachloride*

SAMPLING AND ANALYSIS INFORMATION

Monitor Sampling Rate	*26.5 cm^3/min.*
Recovery Coefficient	*1.02 in CS_2*
Upper Exposure Limit (1)	*3000 µg (298 ppm-hours)*

COMPOUND PROPERTIES AND DATA

Molecular Weight	*153.82*
Published Diffusion Constant (2)	*0.0828 cm^2/sec.*
Density	*1.5942 (20°C)*
T.W.A. (TLV)	*10 ppm*

SPECIAL CONSIDERATIONS

Sample Storage Precautions	*None*
Humidity Effects	*Upper Exposure Limit Slightly Reduce*
The Upper Exposure Limit at *85* % R.H. is	*298 ppm-hours*
Ceiling Level Monitoring (3)	*Not Recommended*

CALCULATION PROCEDURE

A = mass of analyte in micrograms
B = sampling time in minutes
Substitute A & B into equations below:

$$\frac{mg}{m^3} = \frac{37.74 \times A}{\text{recovery coefficient} \times B} = \frac{37.00 \times A}{B}$$

$$ppm\ (4) = \frac{6.00 \times A}{\text{recovery coefficient} \times B} = \frac{5.88 \times A}{B}$$

Footnotes:

(1) This number is the highest concentration of the compound actually measured by the 3M Lab.
(2) Diffusion constants are provided for general interest. They are not required in the calculation procedure.
(3) A minimum sampling time of 15 minutes is required.
(4) ppm based on 25°C. 760 mm Hg.

3M BRAND ORGANIC VAPOR MONITOR
PRODUCT NO. 3500

Qualification Data for Chloroform

SAMPLING AND ANALYSIS INFORMATION

Monitor Sampling Rate	31.6 cm^3/min.
Recovery Coefficient	0.97 in CS_2
Upper Exposure Limit (1)	3142 µg (340 ppm-hours)

COMPOUND PROPERTIES AND DATA

Molecular Weight	119.38
Published Diffusion Constant (2)	0.0888 cm^2/sec.
Density	1.4984 (15°C)
T.W.A. (TLV)	10 ppm

SPECIAL CONSIDERATIONS

Sample Storage Precautions	None
Humidity Effects	Upper Exposure Limit Slightly Reduced
The Upper Exposure Limit at 85 % R.H. is	340 ppm-hours
Ceiling Level Monitoring (3)	Not Recommended

CALCULATION PROCEDURE

A = mass of analyte in micrograms
B = sampling time in minutes
Substitute A & B into equations below:

$$\frac{mg}{m^3} = \frac{31.65 \times A}{\text{recovery coefficient} \times B} = \frac{32.63 \times A}{B}$$

$$ppm\ (4) = \frac{6.48 \times A}{\text{recovery coefficient} \times B} = \frac{6.68 \times A}{B}$$

Footnotes:
(1) This number is the highest concentration of the compound actually measured by the 3M Lab.
(2) Diffusion constants are provided for general interest. They are not required in the calculation procedure.
(3) A minimum sampling time of 15 minutes is required.
(4) ppm based on 25 °C. 760 mm Hg.

3M BRAND ORGANIC VAPOR MONITOR
PRODUCT NO. 3500

Qualification Data for Methyl Chloroform (1,1,1-Trichloroethane)

SAMPLING AND ANALYSIS INFORMATION

Monitor Sampling Rate	28.0 cm^3/min.
Recovery Coefficient	1.02 in CS_2
Upper Exposure Limit [1]	4700 µg (1800 ppm-hours)

COMPOUND PROPERTIES AND DATA

Molecular Weight	133.41
Published Diffusion Constant [2]	0.0794 cm^2/sec.
Density	1.3390 (20°C)
T.W.A. (TLV)	350 ppm

SPECIAL CONSIDERATIONS

Sample Storage Precautions	None
Humidity Effects	Upper Exposure Limit Slightly Reduced
The Upper Exposure Limit at -- % R.H. is	--
Ceiling Level Monitoring [3]	Recommended

CALCULATION PROCEDURE

A = mass of analyte in micrograms
B = sampling time in minutes
Substitute A & B into equations below:

$$\frac{mg}{m^3} = \frac{35.71 \times A}{\text{recovery coefficient} \times B} = \frac{35.01 \times A}{B}$$

$$ppm\ [4] = \frac{6.54 \times A}{\text{recovery coefficient} \times B} = \frac{6.42 \times A}{B}$$

Footnotes:

(1) This number is the highest concentration of the compound actually measured by the 3M Lab.
(2) Diffusion constants are provided for general interest. They are not required in the calculation procedure.
(3) A minimum sampling time of 15 minutes is required.
(4) ppm based on 25 °C. 760 mm Hg.

R-35QDS-9

3M 107462

3M BRAND ORGANIC VAPOR MONITOR
PRODUCT NO. 3500

Qualification Data for 1,1,2-Trichloroethane

SAMPLING AND ANALYSIS INFORMATION

Monitor Sampling Rate	27.1 $cm^3/min.$
Recovery Coefficient	1.00 in CS_2
Upper Exposure Limit (1)	To Be Determined

COMPOUND PROPERTIES AND DATA

Molecular Weight	133.41
Published Diffusion Constant (2)	0.0792 $cm^2/sec.$
Density	1.4390 (20°C)
T.W.A. (TLV)	10 ppm

SPECIAL CONSIDERATIONS

Sample Storage Precautions	None
Humidity Effects	Upper Exposure Limit Slightly Reduced
The Upper Exposure Limit at - % R.H. is	-
Ceiling Level Monitoring (3)	Recommended

CALCULATION PROCEDURE

A = mass of analyte in micrograms
B = sampling time in minutes
Substitute A & B into equations below:

$$\frac{mg}{m^3} = \frac{36.90 \times A}{\text{recovery coefficient} \times B} = \frac{36.90 \times A}{B}$$

$$ppm\ (4) = \frac{6.76 \times A}{\text{recovery coefficient} \times B} = \frac{6.76 \times A}{B}$$

Footnotes:
(1) This number is the highest concentration of the compound actually measured by the 3M Lab.
(2) Diffusion constants are provided for general interest. They are not required in the calculation procedure.
(3) A minimum sampling time of 15 minutes is required.
(4) ppm based on 25°C. 760 mm Hg.

3M BRAND ORGANIC VAPOR MONITOR
PRODUCT NO. 3500

Qualification Data for *Trichloroethylene*

SAMPLING AND ANALYSIS INFORMATION

Monitor Sampling Rate	*28.0 cm^3/min.*
Recovery Coefficient	*1.00 in CS_2*
Upper Exposure Limit (1)	*20.3 mg (2250 ppm-hours)*

COMPOUND PROPERTIES AND DATA

Molecular Weight	*131.39*
Published Diffusion Constant (2)	*0.0875 cm^2/sec.*
Density	*1.462 (20°C)*
T.W.A. (TLV)	*100 ppm*

SPECIAL CONSIDERATIONS

Sample Storage Precautions	*None*
Humidity Effects	*Upper Exposure Limit Reduced*
The Upper Exposure Limit at *85* % R.H. is	*1600 ppm-hours*
Ceiling Level Monitoring (3)	*Recommended*

CALCULATION PROCEDURE

A = mass of analyte in micrograms
B = sampling time in minutes
Substitute A & B into equations below:

$$\frac{mg}{m^3} = \frac{35.71 \times A}{\text{recovery coefficient} \times B} = \frac{35.71 \times A}{B}$$

$$ppm\ (4) = \frac{6.65 \times A}{\text{recovery coefficient} \times B} = \frac{6.65 \times A}{B}$$

Footnotes:

(1) This number is the highest concentration of the compound actually measured by the 3M Lab.
(2) Diffusion constants are provided for general interest. They are not required in the calculation procedure.
(3) A minimum sampling time of 15 minutes is required.
(4) ppm based on 25°C. 760 mm Hg.

3M BRAND ORGANIC VAPOR MONITOR
PRODUCT NO. 3500

Qualification Data for *Vinyl Chloride*

SAMPLING AND ANALYSIS INFORMATION

Monitor Sampling Rate	*40.7 cm^3/min.*
Recovery Coefficient	*0.90 in CS_2*
Upper Exposure Limit [1]	*168 µg (30 ppm-hours)*

COMPOUND PROPERTIES AND DATA

Molecular Weight	*62.50*
Published Diffusion Constant [2]	*Not Available*
Density	*-*
T.W.A. (TLV)	*1.0 ppm*

SPECIAL CONSIDERATIONS

Sample Storage Precautions	*None*
Humidity Effects	*Upper Exposure Limit Substantially Reduced*
Th Upper Exposure Limit at *90* % R.H. is	*5 ppm-hours*
Ceiling Level Monitoring [3]	*Not Recommended*

CALCULATION PROCEDURE

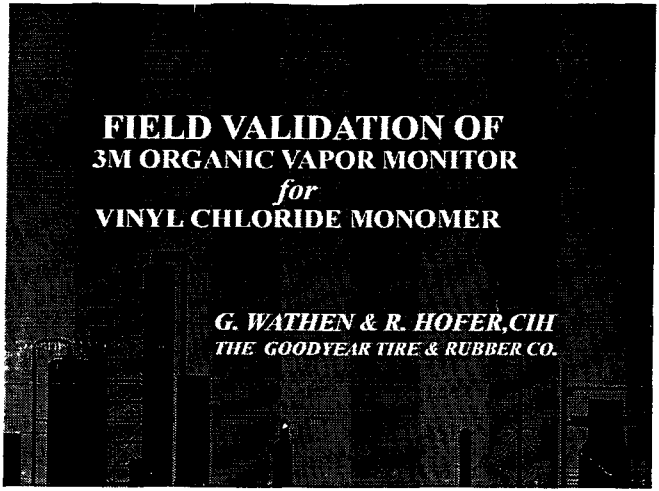
A = mass of analyte in micrograms
B = sampling time in minutes
Substitute A & B into equations below:

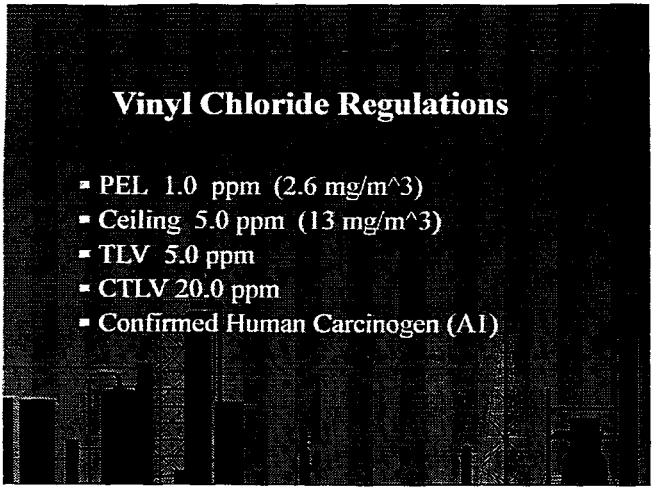
$$\frac{mg}{m^3} = \frac{24.59 \times A}{\text{recovery coefficient} \times B} = \frac{27.32 \times A}{B}$$

$$\text{ppm}^{(4)} = \frac{9.62 \times A}{\text{recovery coefficient} \times B} = \frac{10.69 \times A}{B}$$

Footnotes:

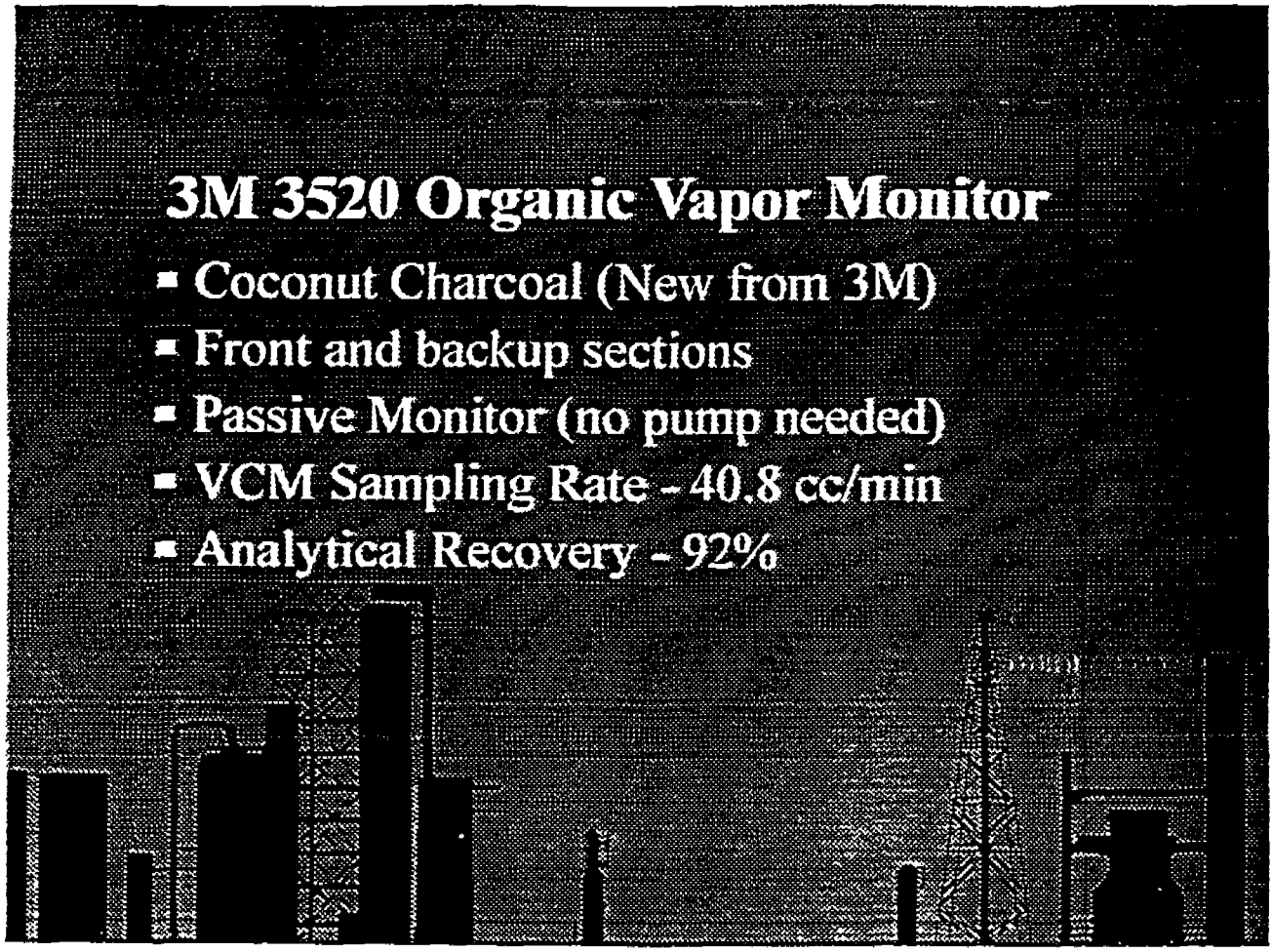
(1) This number is the highest concentration of the compound actually measured by the 3M Lab.
(2) Diffusion constants are provided for general interest. They are not required in the calculation procedure.
(3) A minimum sampling time of 15 minutes is required.
(4) ppm based on 25 °C. 760 mm Hg.


FIELD VALIDATION OF
3M ORGANIC VAPOR MONITOR
for
VINYL CHLORIDE MONOMER
G. WATHEN & R. HOFER,CIH
THE GOODYEAR TIRE & RUBBER CO.



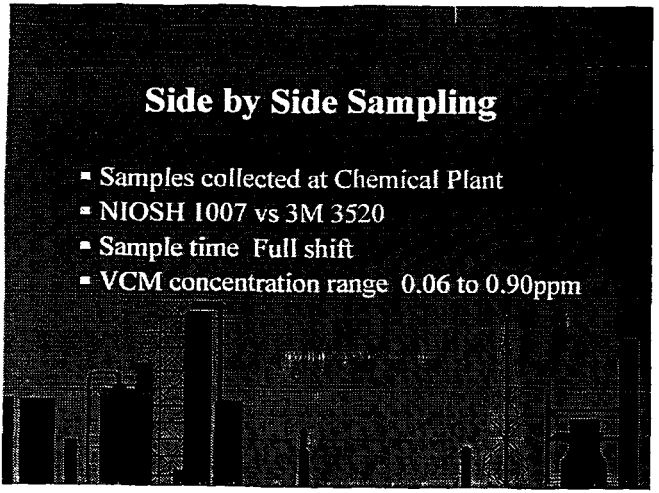
The potential risk of exposure to vinyl chloride monomer, a colorless gas that liquidies upon freezing, causes concern for the health and safety of workers who are involved with this material. The monitoring of both employee and work place environment is necessary to ensure that exposure remains below the setback limits and complies with the law. Vinyl chloride OSHA regulations states that the "permissible exposure limit-PEL is 1ppm, with a ceiling value of 5ppm. American Conference of Governmental Industrial Hygienists ACGIH has a threshold limit value - TLV of 5ppm with a ceiling value of 20ppm.

With [illegible] has been classified [illegible] - a confirmed [illegible] on evidence from epidemiology studies or [illegible] animals

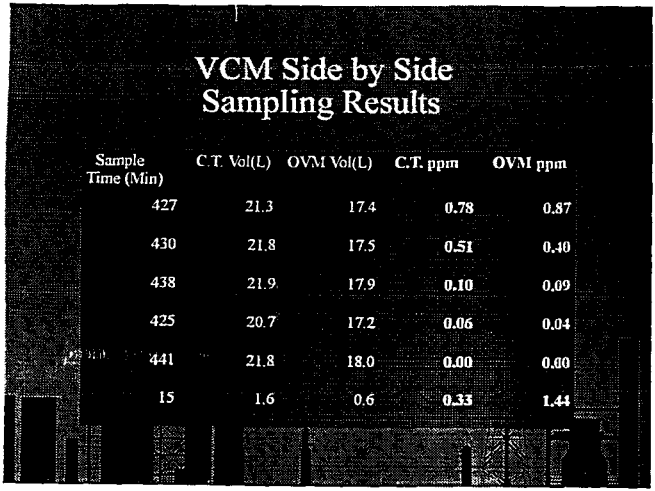


The current method to monitor vinyl chloride monomer, NIOSH 1007, uses a coconut charcoal solid sorbent tube as the sampler in conjunction with a pump. Because of the constraints of active methods for monitoring vinyl chloride, a more practical quantitative sampler was desired. A coconut charcoal organic vapor monitor - new from 3M - was tested. This 3520 OVM has both front and back sections. The passive monitor eliminates the bulky, expensive pump that needs calibration.

[illegible] the sampling rate calculated by 3M as 41.1 cc/min the [illegible] for vinyl chloride spiked on the new OVM [illegible] at the 3M target level of 1PPM. Set at 1.0 the [illegible] at twice the target level. This good [illegible] in the lab led to the next tests at the [illegible]

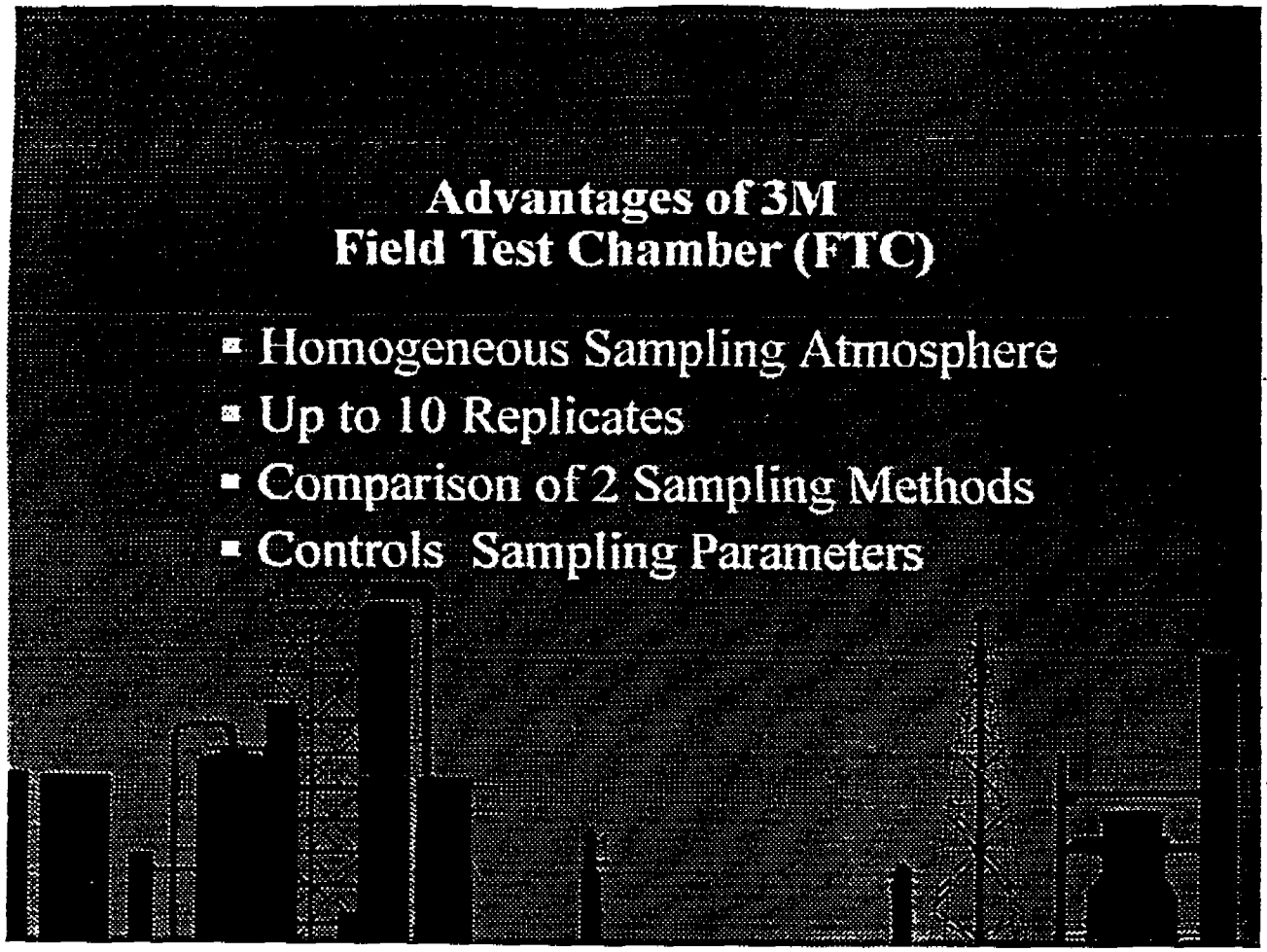


To test the passive monitor in a field atmosphere, a series of side-by-side samples were collected at the Chemical Plant. The samples were collected on coconut charcoal sorbent tubes as outlined in NIOSH 1007 and on the new 3M 3520 OVM passive monitor. A full shift approximately 8 hours, was used for the sampling. A short term sample was also collected. Several locations in the Chemical Plant were chosen covering a vinyl chloride monomer range from .06 to .90ppm



The results of the side-by-side sampling in the Chemical Plant for vinyl chloride monomer show that both the sensitivity and selectivity of the coconut OVM sampling media is in good agreement of the charcoal tube used in the NIOSH 1007 method when sampling at the recommended pump rate of 50 cc min. The concentration of the vinyl chloride monomer recovered for a full shift on both the charcoal tube and the coconut OVM at approximately the PEL (1ppm), 1/2 PEL (0.5ppm) and at 1 10 PEL or less (0.1 ppm) are shown, along with the blank. All levels have good correlation.

The short term (15 min.) sampling result indicate that the coconut OVM is not suitable.



Following the side-by-side sampling, a field test chamber was next used at the Chemical Plant to verify that both media charcoal tubes and coconut OVM) had the identical homogenous sampling atmosphere. The field test chamber, designed by 3M, allows up to 11 replicate samples to be taken by using the multiple sampling ports. A comparison of 2 sampling methods - the charcoal tube and passive OVM can be made with the field test chamber. The chamber was used at 2 different locations so the vinyl chloride monomer concentration varied.

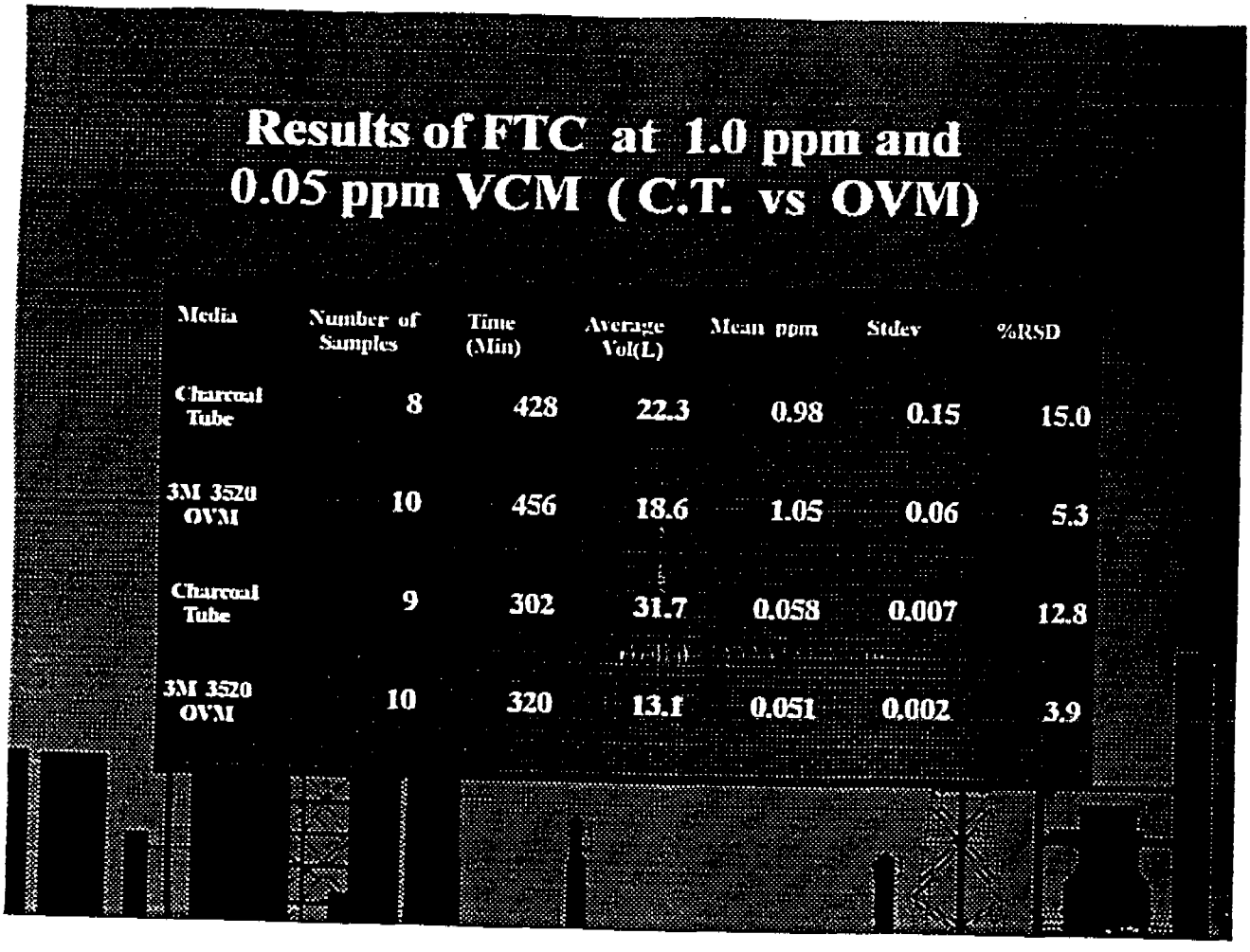
The next slide illustrates the field test chamber.

Here we see the field test chamber which is made of plexiglas.
- Sampling ports for the charcoal tubes with pumps - up to 5 were used on each chamber.

- 5 OVM's in the chamber - all passive dosimeters were placed in parallel direction.

Air was continuously pulled through the chamber by a variable speed fan at a predetermined linear face velocity (150 ft/min). The velocity was measured using a magnahelic monometer.

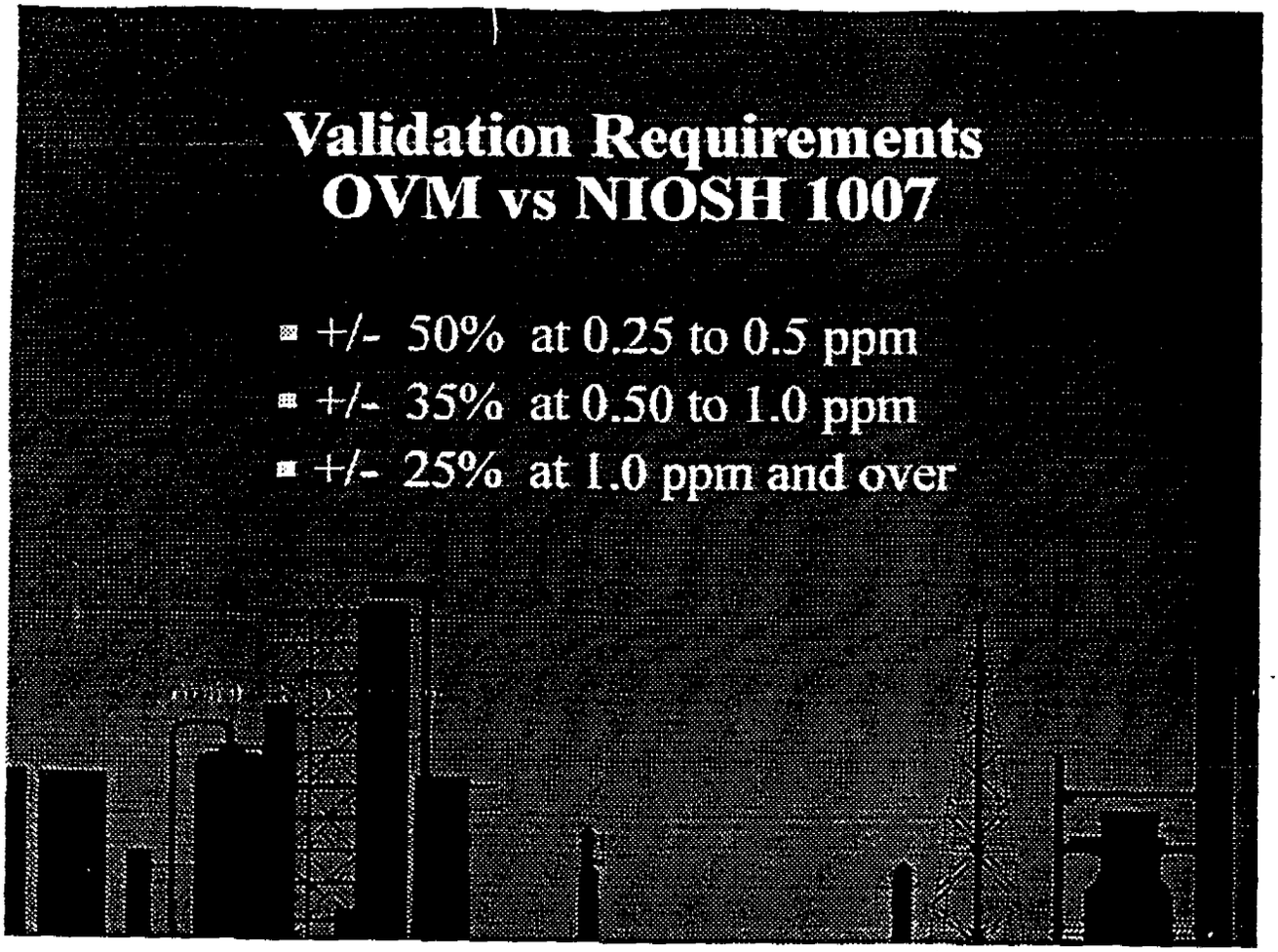
Using the field test chamber, both passive monitor OVM's and charcoal tubes were exposed to identical atmospheric conditions.



The results of the field test chamber sampling at the 2 different locations in the chemical plant are shown in this chart.

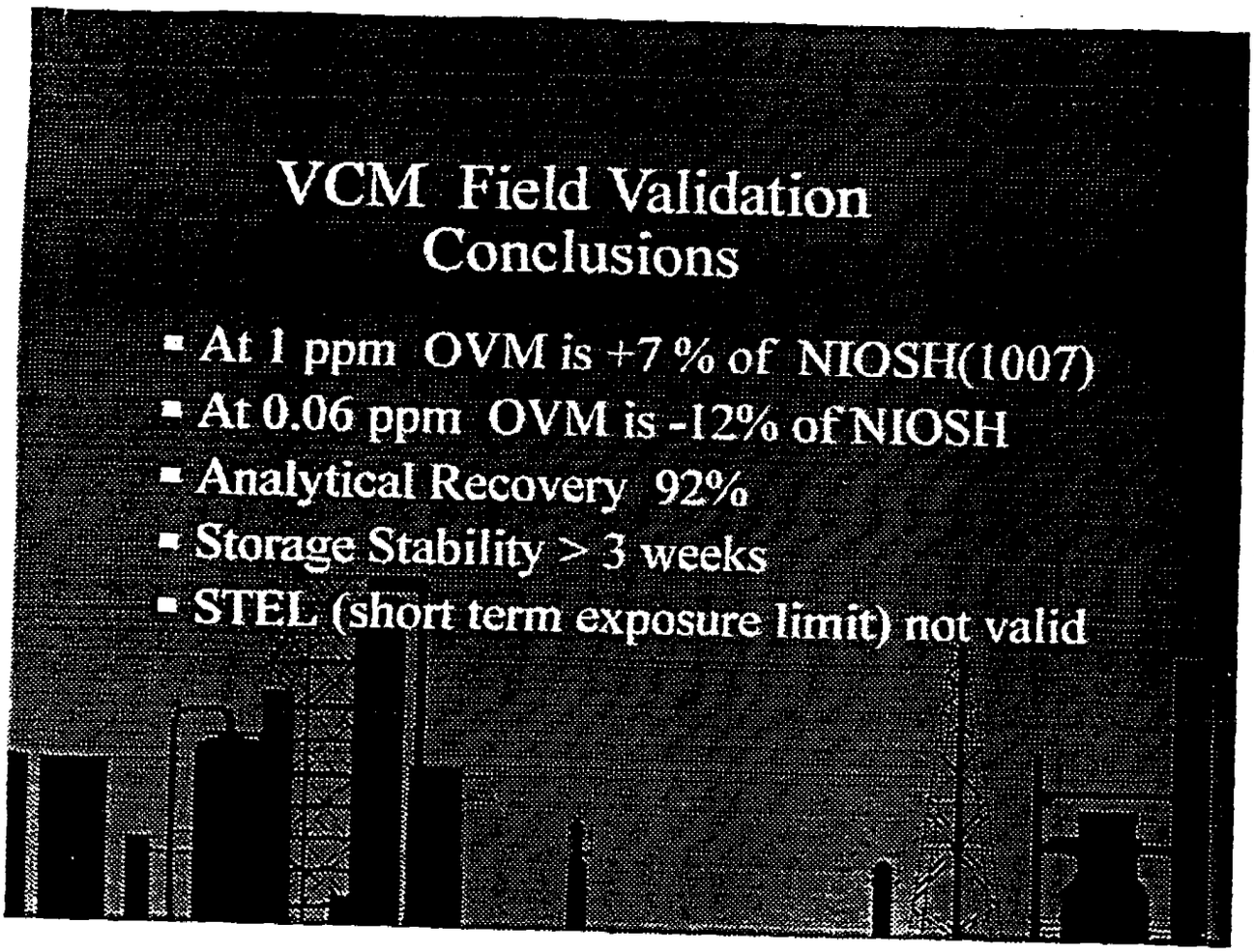
At the first location at the PEL 1ppm concentration level - 8 charcoal tubes had a mean ppm of 1.98 with a std dev of 0.15 and a RSD of 15%. The 10 3520-OVM's had a mean ppm of 1.05 with a std dev of 0.06 and a RSD of 5.3%.

At the second location at the 1/2 the PEL 0.05ppm the concentration level for 9 charcoal tubes had a mean ppm of 0.058 with a std dev of 0.007 and a RSD of 12.8%. The 10 OVM's had a mean ppm of 0.051 with a std dev of 0.002 and a RSD of 3.9%.



NIOSH protocol for monitoring and measurement validation states that the new method has an accuracy compared to the current acceptable NIOSH method of not less than:

- +/- 50% at 0.25 - 0.5 ppm
- +/- 35% at 0.5 - 1.0 ppm
- +/- 25% at 1.0 ppm and over

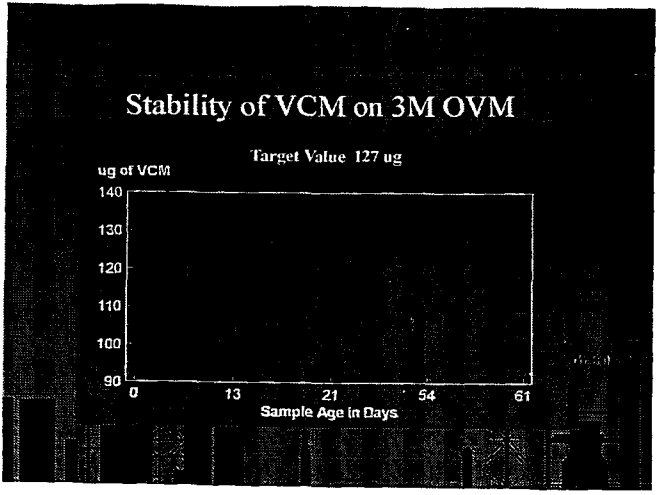


The NIOSH protocol for the validation of passive monitor passed the accuracy requirements - at 1ppm the OVM is -7% of NIOSH 1007 method and at 0.06ppm the OVM is -12% of NIOSH 1007.

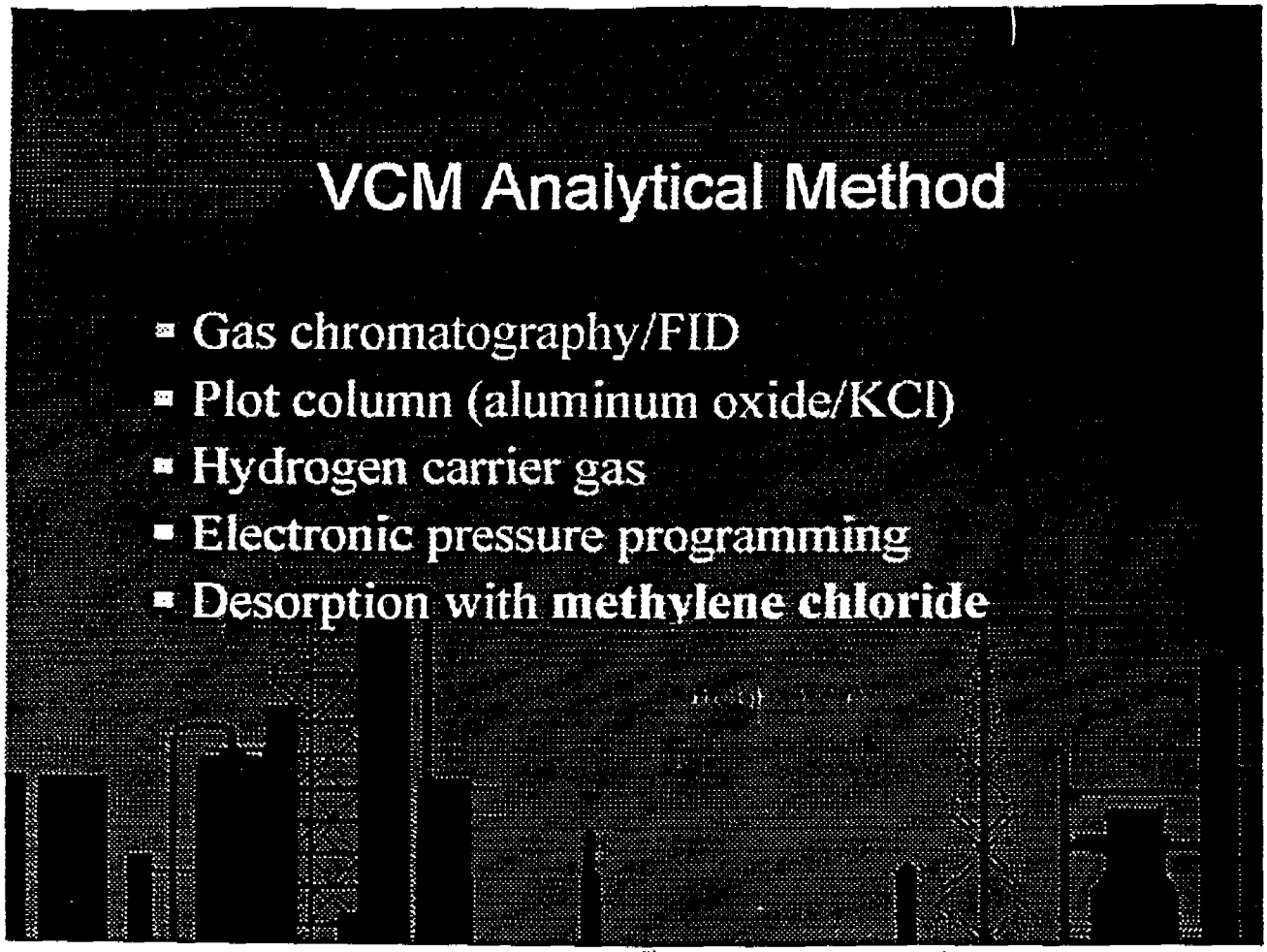
Analytical recovery is 92% >75% is required .

Storage stability of the OVM is 3 weeks (2 weeks-minimum are required . Stability plot shown in next slide.

The STEL is a 15 min exposure limit , however it is not valid.



The 3M 3521 OVM monitors were spiked with a gas vapor of the vinyl chloride monomer. The OVM's were stored in a refrigerator and analyzed weekly for VCM. After 3 weeks, the storage loss of vinyl chloride monomer was not acceptable.



The analytical method developed to measure vinyl chloride monomer used for the field validation of the passive 3M coconut OVM monitor included the following:

1. Gas chromatography with a flame ionization detector (FID).
2. Plot column (porous layer open tubular column; coated with aluminum oxide and deactivated with potassium chloride (KCl) Ideal for separation of light hydrocarbons.
3. Hydrogen carrier gas
4. Electronic pressure programming-EPP-better resolution, improved detection limits, faster analysis. Initial pressure pulse of 35 psi/min.
5. Methylene chloride used to desorb OVM.

3M BRAND ORGANIC VAPOR MONITOR
PRODUCT NO. 3500

Qualification Data for Tetrachloroethylene*

SAMPLING AND ANALYSIS INFORMATION

Monitor Sampling Rate	28.9 cm^3/min.
Recovery Coefficient	1.00
Upper Exposure Limit (1)	36.0 Mg (3060 ppm-hr)

COMPOUND PROPERTIES AND DATA

Molecular Weight	165.85
Published Diffusion Constant (2)	None
Density	1.6226 (20°C)
T.W.A. (TLV)	100 ppm (681 mg/m^3)

SPECIAL CONSIDERATIONS

Sample Storage Precautions	None
Humidity Effects	Upper exposure limit slightly reduced
The Upper Exposure Limit at 85 % R.H. is	36.0 Mg (3060 ppm-hr)
Ceiling Level Monitoring (3)	Recommended

CALCULATION PROCEDURE

A = mass of analyte in micrograms
B = sampling time in minutes
Substitute A & B into equations below:

$$\frac{mg}{m^3} = \frac{34.60 \times A}{\text{recovery coefficient} \times B} = \frac{34.60 \times A}{B}$$

$$ppm\ (4) = \frac{5.10 \times A}{\text{recovery coefficient} \times B} = \frac{5.10 \times A}{B}$$

Footnotes:

(1) This number is the highest concentration of the compound actually measured by the 3M Lab.
(2) Diffusion constants are provided for general interest. They are not required in the calculation procedure.
(3) A minimum sampling time of 15 minutes is required.
(4) ppm based on 25°C. 760 mm Hg.

*Perchloroethylene

3M BRAND ORGANIC VAPOR MONITOR
PRODUCT NO. 3500

Qualification Data for Epichlorohydrin*

SAMPLING AND ANALYSIS INFORMATION

Monitor Sampling Rate	29.8 cm^3/min.
Recovery Coefficient	.94
Upper Exposure Limit (1)	28.8 Mg (4260 ppm-hrs)

COMPOUND PROPERTIES AND DATA

Molecular Weight	92.53
Published Diffusion Constant (2)	None
Density	1.1750 (25°C)
T.W.A. (TLV)	5 ppm (20 mg/m^3)

SPECIAL CONSIDERATIONS

Sample Storage Precautions	None
Humidity Effects	Upper exposure limit slightly reduced
The Upper Exposure Limit at 85 % R.H. is	28.8 Mg (4260 ppm-hr)
Ceiling Level Monitoring (3)	Recommended

CALCULATION PROCEDURE

A = mass of analyte in micrograms
B = sampling time in minutes
Substitute A & B into equations below:

$$\frac{mg}{m^3} = \frac{33.56 \times A}{\text{recovery coefficient} \times B} = \frac{35.70 \times A}{B}$$

$$ppm\ (4) = \frac{8.87 \times A}{\text{recovery coefficient} \times B} = \frac{9.44 \times A}{B}$$

Footnotes:

(1) This number is the highest concentration of the compound actually measured by the 3M Lab.
(2) Diffusion constants are provided for general interest. They are not required in the calculation procedure.
(3) A minimum sampling time of 15 minutes is required.
(4) ppm based on 25°C. 760 mm Hg.

*C_3H_5OCl

1 - Chloro-2,3 - epoxypropane

2 - Chloropropylene oxide

gamma - chloropropylene oxide

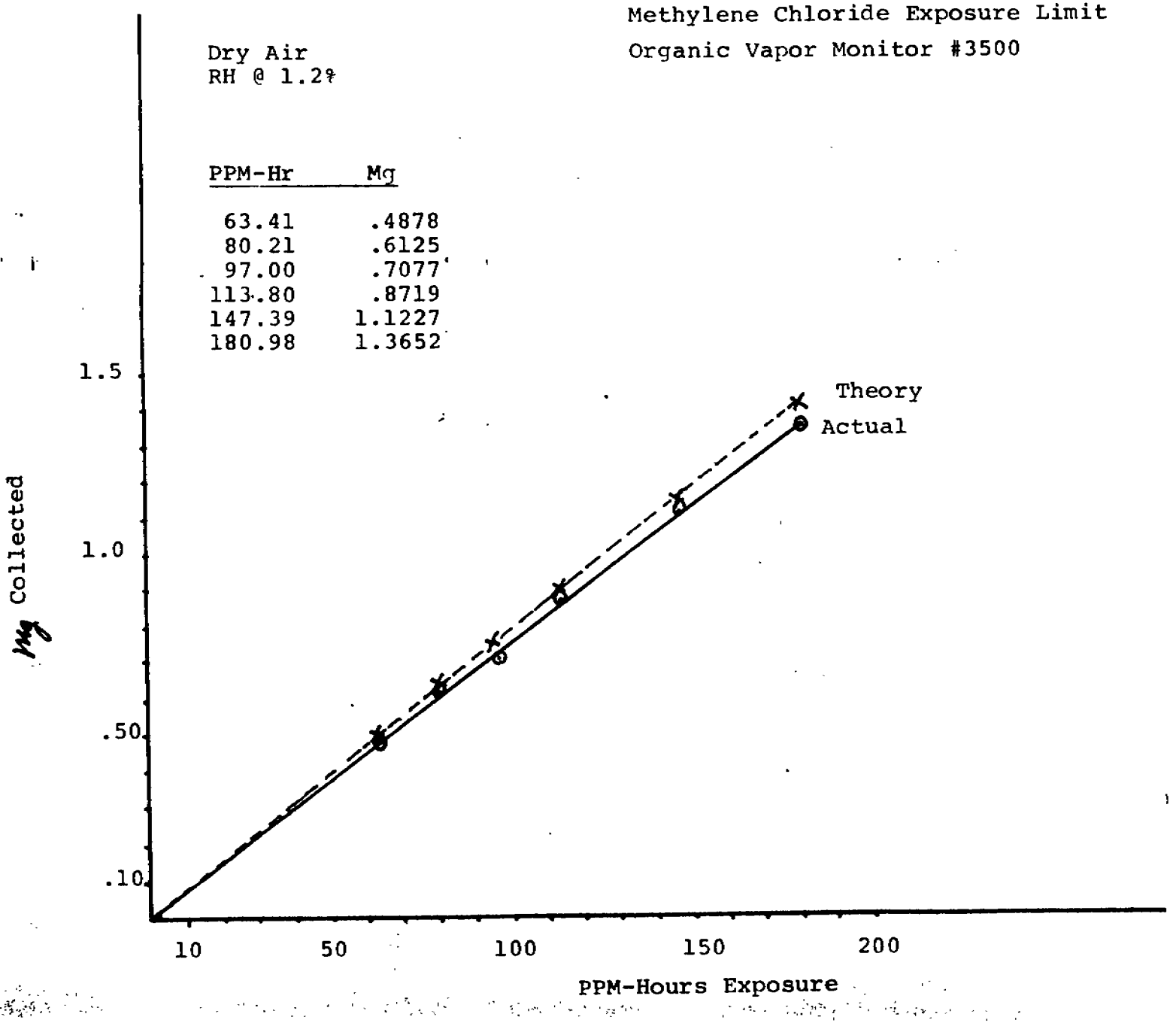
Full Copy (5)

FIGURE 2

Methylene Chloride Exposure Limit
Organic Vapor Monitor #3500

Dry Air
RH @ 1.2%

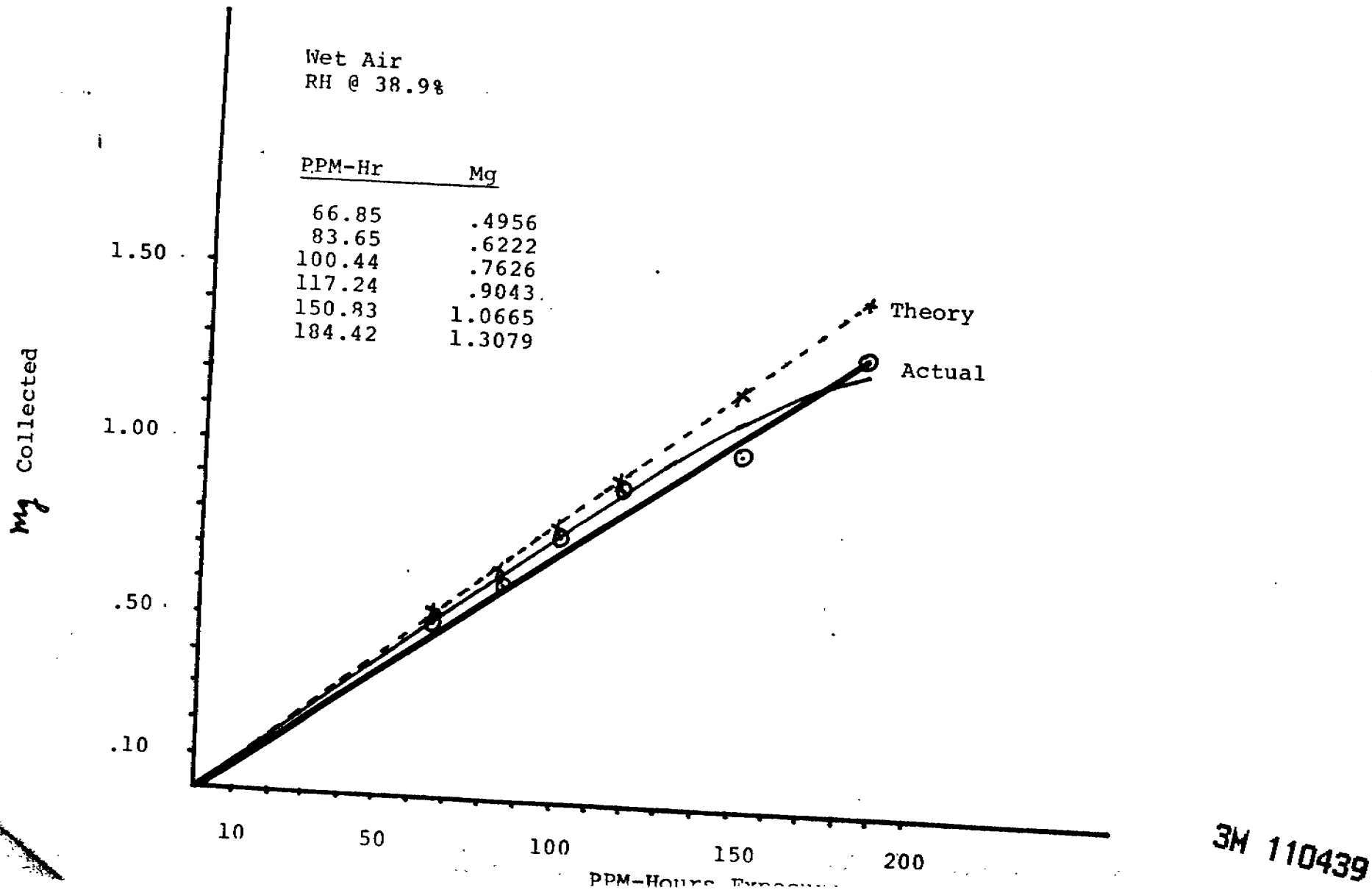
PPM-Hr	Mg
63.41	.4878
80.21	.6125
97.00	.7077
113.80	.8719
147.39	1.1227
180.98	1.3652



3M 110438

FIGURE 3

Methylene Chloride Exposure Limit
Organic Vapor Monitor #3500



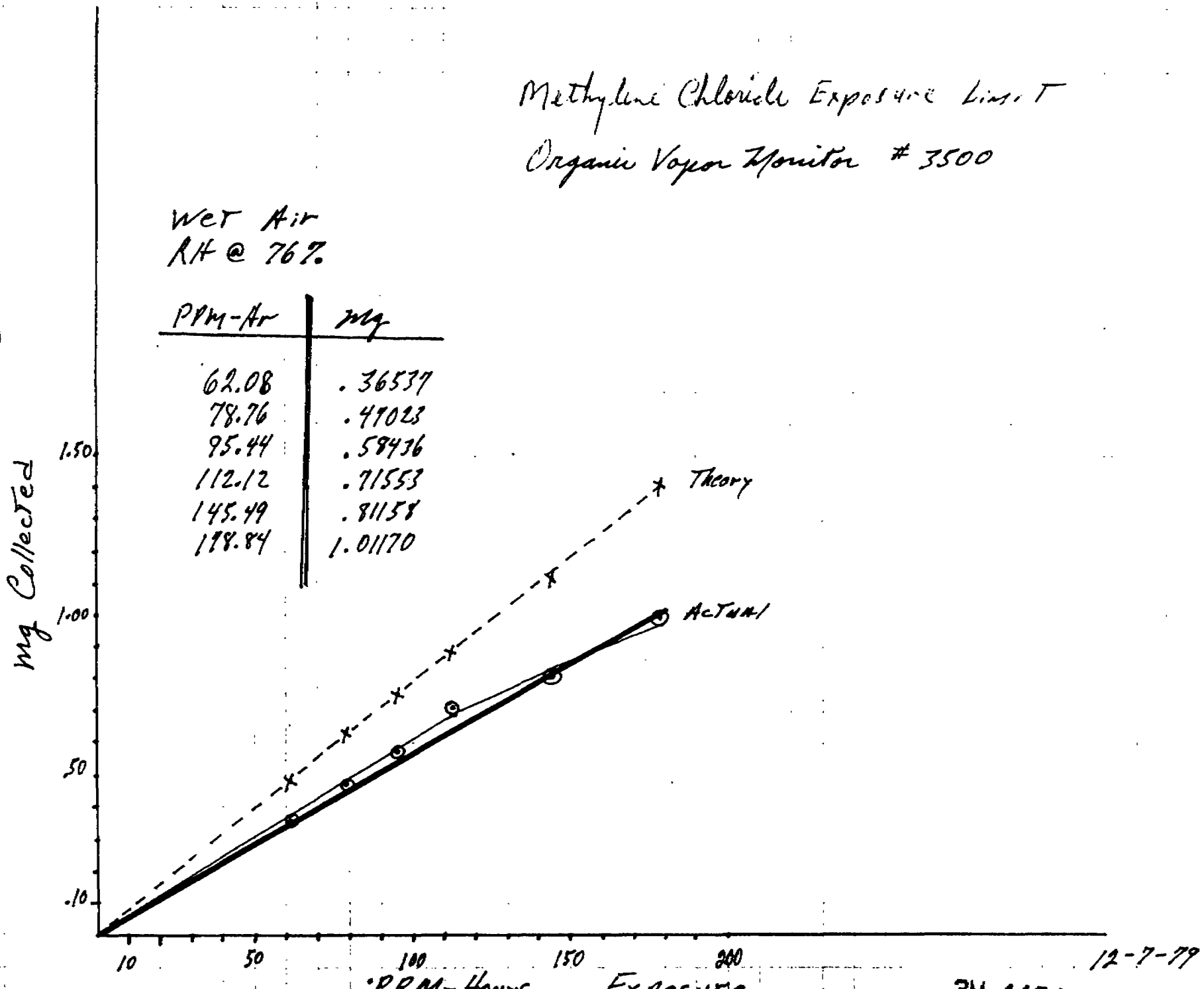
3M 110439

Methylene Chloride Exposure Limit

Organic Vapor Monitor # 3500

Wet Air
RH @ 76%

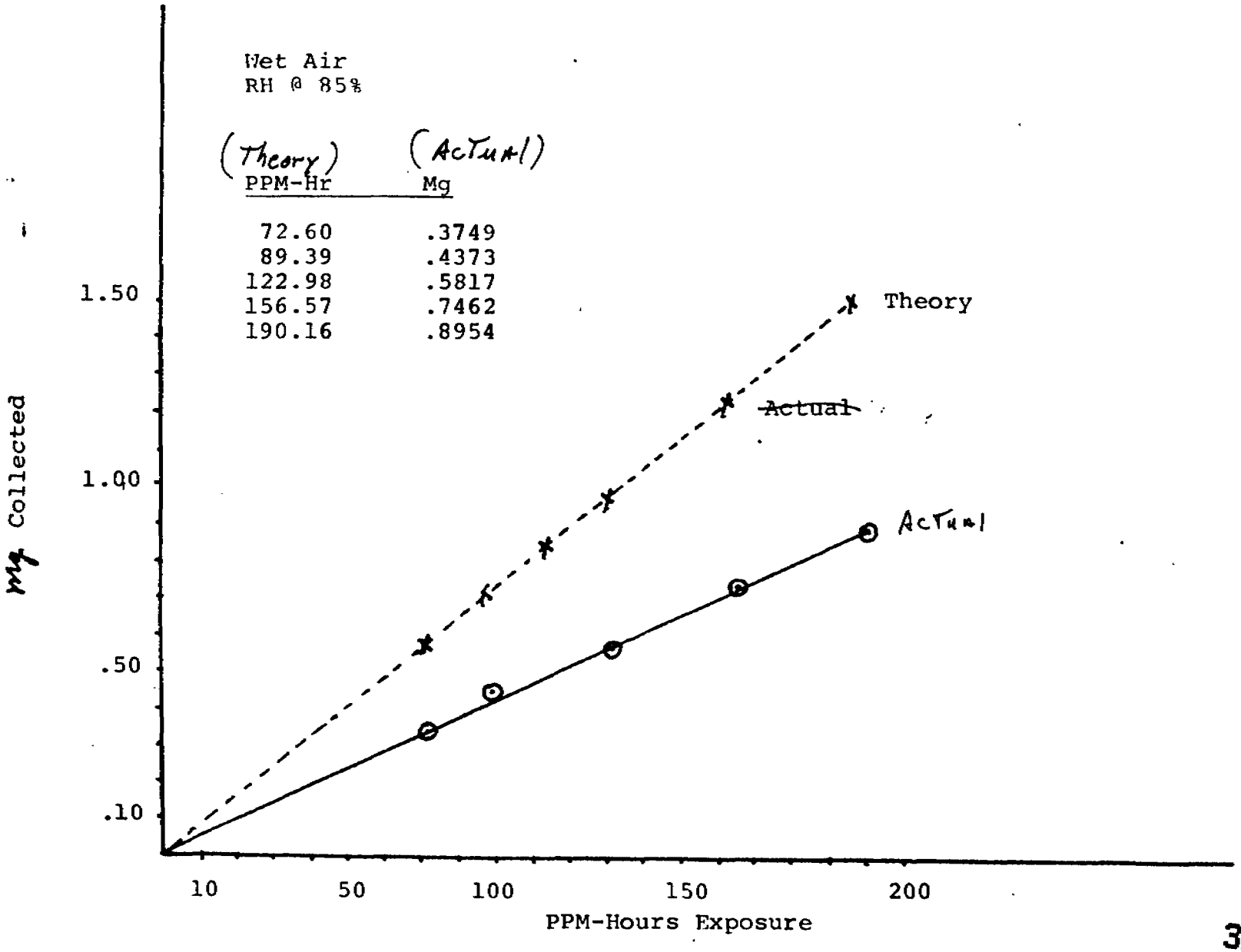
PPM-Hr	mg
62.08	.36537
78.76	.47023
95.44	.58436
112.12	.71553
145.49	.81158
198.84	1.01170



3M 110440

FIGURE 4

Methylene Chloride Exposure Limit
Organic Vapor Monitor #3500



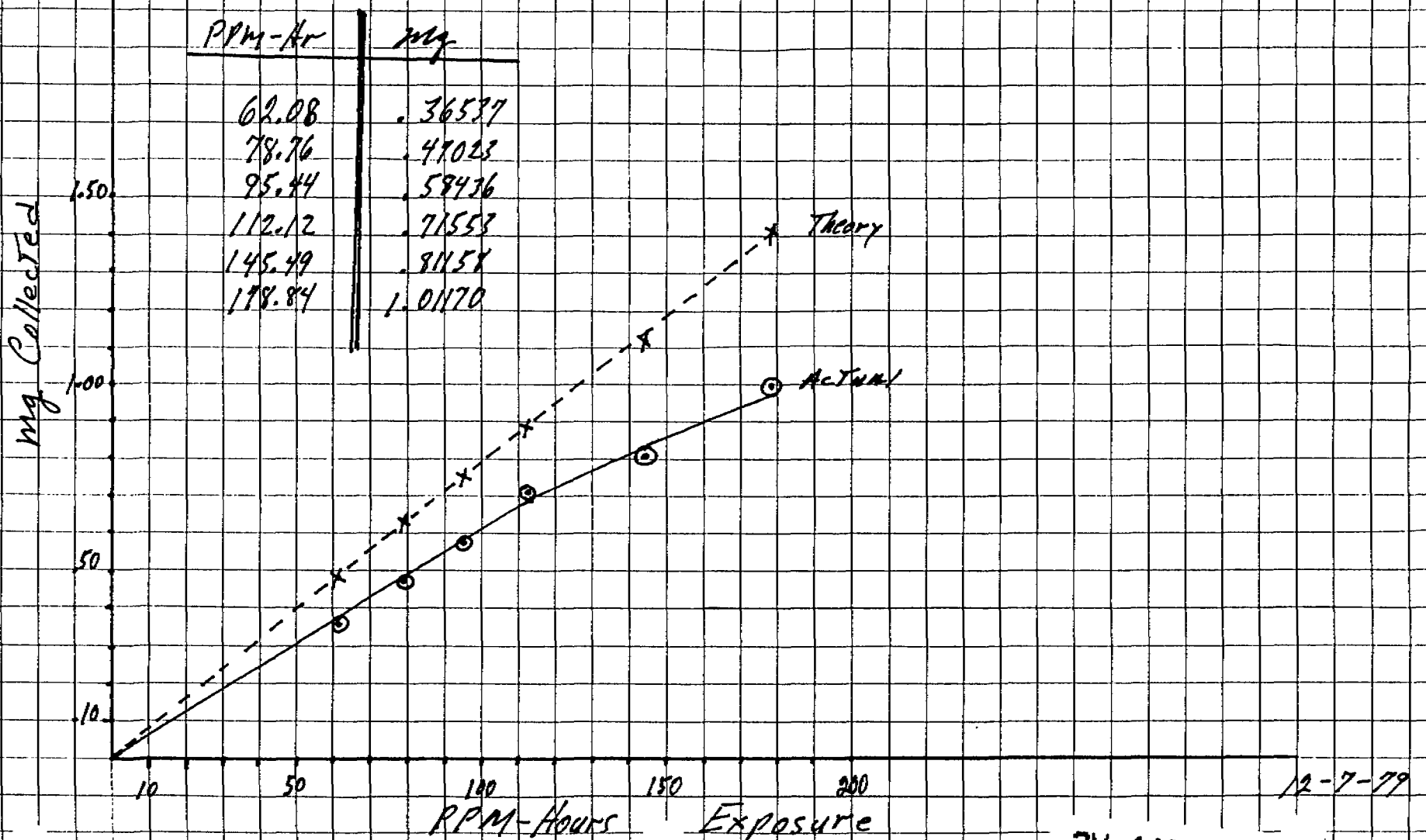
3M 110441

Methylene Chloride Exposure Limit

Organic Vapor Monitor # 3500

Wet Air
RH @ 76%

PPM-Hr	mg
62.08	.36537
78.76	.47023
95.44	.58436
112.12	.71553
145.49	.81458
178.84	1.01170



3M 110442

Long Term Sampling With Diffusion Monitors

Donald J. Larsen and Robert A. Weber
OH&ESD, 3M Company

INTRODUCTION

Industrial hygiene is the science of recognizing, evaluating and controlling workplace hazards. Monitoring the environment is necessary to determine whether exposures are within safe guidelines or whether engineering controls or personal protective equipment are necessary.

Monitoring for gases and vapors typically requires a battery operated pump with sorbent tubes or impingers. Monitors based on principles of diffusion have been shown to have comparable accuracy and have advantages over active sampling in many situations. The amount of a compound collected on a monitor based on the laws of diffusion can be described by the following formula:

$$W = (DA/L)Ct$$

where W is the weight collected, D is the diffusion coefficient, A is the cross-sectional area, L is the diffusion pathlength, C is the concentration and t is the sampling time. The DA/L term has the units of volume/time and can be treated as a sampling rate. The sampling rate for battery operated pumps can be varied from a few mL/min to a L/min. Sampling rates for diffusion monitors depend on the monitor geometry and the diffusion coefficient for the compound. The 3M Company manufactures diffusion monitors for Organic Vapors, Formaldehyde, Ethylene Oxide and Mercury. Typical sampling rates for the 3M organic vapor monitor range from 20 to 40 mL/min. The sorbent in the OVM is activated carbon which has a high surface area due to the microporous structure which is available for adsorption.

Historically diffusion monitors have been validated for monitoring the working environment for full work shifts of 8 hours. We have also shown that our organic vapor monitors can be used to monitor sampling times of 15 minutes to evaluate Short Term Exposure Limits (STELs). Recent concern with indoor air quality, environmental emissions and hazardous waste disposal gives rise to situations where monitoring for extended periods is desirable.

Active sampling with battery operated pumps and sorbent tubes is difficult or impossible for many situations where extended sampling periods are required.

Many lab and field evaluations by 3M and others have been performed over the last 20 years to validate the use of diffusion monitors for work shift sampling. Studies comparing OVMs with charcoal tubes and validation of sampling rates have given most industrial hygienists the confidence to use diffusion monitors to evaluate 8 hour TWA sampling situations.

REFERENCES

3M Organic Vapor Monitor Sampling Rate Validation Protocol

Anders, L. W., and H. E. Mullins: Comparison of Diffusional Organic Vapor Monitors with Charcoal Tubes for Sampling Laboratory Challenges to Contaminant Mixtures

Anders, L. W., H. E. Mullins and P. L. Sullivan: Organic Vapor Monitor with Backup Section

When the capacity is poor and uptake rates depart from linearity as shown in the following graphs the 3520 monitor that has a backup section of charcoal can be used to extend sampling times.

In 1990, 3M presented a paper at the ACS meeting in Boston to show that our organic vapor monitors are also valid for STEL sampling.

Pieper, Richard M., Donald J. Larsen, and Patricia A. Ishaug: STEL Sampling Using Diffusional Monitors, American Chemical Society Meeting, Boston, MA, April, 1990.

The following table shows a comparison of 1000 ppm acetone collected on charcoal tubes with monitors. The monitors and charcoal tubes indicate the same concentration.

STEL SAMPLING FOR ACETONE
3M 3520 ORGANIC VAPOR MONITOR

TIME (MIN)	MONITOR (PPM)	CHARCOAL TUBE (PPM)
7 1/2	1085 +/-68 (6.3%)	1057 +/-15 (1.4%)
15	1134 +/-59 (5.2%)	1099 +/-42 (3.9%)
15	1092 +/-83 (7.6%)	1117 +/-33 (2.9%)
22 1/2	1136 +/-60 (5.2%)	1164 +/-11 (1.0%)

Today we will present data to show that the OVM monitors can be used for extended sampling periods as well. A few previous references to the use of our monitors are shown below. They exposed the 3M 3500 monitors to very low concentrations (<50 ppb) for three weeks. They found the monitors acceptable but did not study the effects of reverse diffusion.

REFERENCES

Epstein, Paul S., et al: Experiences Using Passive Monitors to Measure Volatile Organic Compounds During Indoor and Ambient Air Quality Surveys, American Industrial Hygiene Conference, 1990.

Cohen, Martin A., et al: The Validation of a Passive Sampler for Indoor and Outdoor Concentrations of Volatile Organic Compounds, J. Air Waste Manage. 40:993(1990).

Validation of a diffusion monitor must address the following factors whether the sampling period is 8 hours, 15 minutes or 1 week:

- Recovery
- Analytical sensitivity
- Capacity (reverse diffusion)
- Linear uptake rate
- Orientation
- Temperature
- Face velocity
- Interferences
- Storage

Recovery can vary with loading. This is especially true for oxygenated compounds which may have lower recoveries at very low loadings.

For indoor air quality investigations the concentrations may be very low, so long sampling times may be necessary to accumulate enough for analysis. Epstein and Cohen found it necessary to use GC/MS/SIM to quantitatively analyze monitors at the low ppb levels even with long sampling times.

Reverse diffusion (loss of previously adsorbed solvent during the sampling period) is the major concern which needs to be addressed for long term sampling. This manifests itself in a sampling rate which appears to be lower than predicted. These effects can be studied by using the 3520 monitor which has a backup section while exposing the monitor at levels which would not exceed the expected capacity for the primary layer.

Effects due to orientation, temperature, face velocity, interferences and storage would be expected to be similar to that for workshift sampling and were not further tested in this study.

EXPERIMENTAL

A source of compressed air is passed over heated water to provide a known humidity. We maintained a relative humidity of 30% at 23 C. Organic solvent is vaporized into the air stream to create a known concentration. For high concentrations we use a syringe pump to inject liquid onto a heated aluminum block. For the low concentrations in these studies we used a 3.7 mL septum capped vial having an appropriate sized hole (usually 1 mm diameter) in the septum. The challenge concentration is then passed through a Plexiglas chamber (5" x 5" x 21") containing the monitors which allows simultaneous sampling through sorbent tubes. The challenge concentration may also be monitored by portable infrared analyzer, flame ionization detector or gas chromatograph.

A challenge air flow of 90 Lpm creates a face velocity of 19 feet per minute (fpm) and 140 Lpm creates a face velocity 29 fpm in our chamber. We generally recommend a minimum face velocity of 25 fpm to avoid starvation effects.

We wished to evaluate our monitors for long exposure times to low concentrations of solvents to determine whether the published sampling rates in our Sampling and Analytical Guide would remain valid under these conditions. Laboratory tests were run using toluene, acetone, 1,1,1-trichloroethane, and methylene chloride. A field test evaluated exposure to a mixture of n-butanol and isopropanol.

The compounds selected enabled us to test several classes of compounds having a range of affinity for the activated carbon sorbent. Toluene is held very well. Acetone and methylene chloride are held only weakly. This ability of the sorbent to hold the compound of interest leading to a linear uptake rate is one of the most critical parameters to measure. We used the 3520 monitors which have a backup section for our studies.

The accuracy of a monitor for workplace evaluations is expressed as the following combination of the precision and bias: 2 X Coefficient of Variation + |Bias| $<25\%$.

Typical values for the CV are about 5% and for the bias also about 5% for a typical accuracy of 15% for workshift monitoring.

COMPOUND	EXPOSURE TIME (DAYS)	CONC (PPM)	AMOUNT FOUND (MG)	AMOUNT EXPECTED (MG)	ACCURACY %
Toluene	2 3/4	2.3	1.074	1.088	16.1
1,1,1-TCE	1	2.6	0.61	0.65	15.8
1,1,1-TCE	8	0.45	0.85	0.83	13.4
Acetone	5	2.86	1.767	1.97	17.4

For our first experiment, we chose toluene. If anything could be expected to work, it would be toluene. Charcoal has a high affinity for toluene. The capacity on our monitor is >25 mg. Toluene can also be recovered from charcoal with carbon disulfide with 100% efficiency.
After the 2 3/4 days at 2.3 ppm toluene, three of the monitors were exposed to clean air for 1, 2 or 3 days. No difference was seen in the amounts collected. This shows that back diffusion is not a problem under these conditions. Nothing was found on the backup section for the toluene and 1 day 1,1,1-trichloroethane experiments. For the 8 day 1,1,1-trichloroethane experiment nothing was found on the backup after 4 days and only 1 % after 8 days. For acetone, 16% was found on the backup, which is acceptable as our monitor allows up to 50%.

For our 5th experiment, twenty-one monitors were exposed to methylene chloride at 1.9 ppm for 1 to 5 days. Three monitors were removed each day, separated and capped. A graph of the amount collected vs. time shows that the uptake rate remained linear throughout this exposure. The CV was 4.1% and the bias was +17.1% for an accuracy of 25.3%. Although this is somewhat higher than we usually see for 8 hour samples it is still very good for a compound which has low capacity. For occupational exposures we recommend a maximum of 4 hours sampling where concentrations are allowed to reach or exceed the proposed limit of 25 ppm.

The other six monitors were removed from the exposure chamber after 24 hours and allowed to sit for 24 hours in the laboratory, then reexposed for 24 hours followed by 24 hours at 0 ppm and then another 24 hours in the chamber. These monitors had 72 hours of exposure and collected 95% of the amount collected by the monitors with 72 hours of continuous exposure.

Our 6th experiment was a field test in a 3M pilot plant where we measured the concentration of isopropanol and n-butanol over a 3 day time period. Monitors were exposed for 1, 2 and 3 days. Charcoal tube were taken on Day 1 and Day 3. The results shown in the following table indicate excellent agreement.

COMPOUND	MONITOR PPM	CHARCOAL TUBE PPM
Isopropanol	0.55 +/- 0.07	0.48 +/- 0.11
n-Butanol	0.18 +/- 0.008	0.17 +/- 0.03

CONCLUSIONS

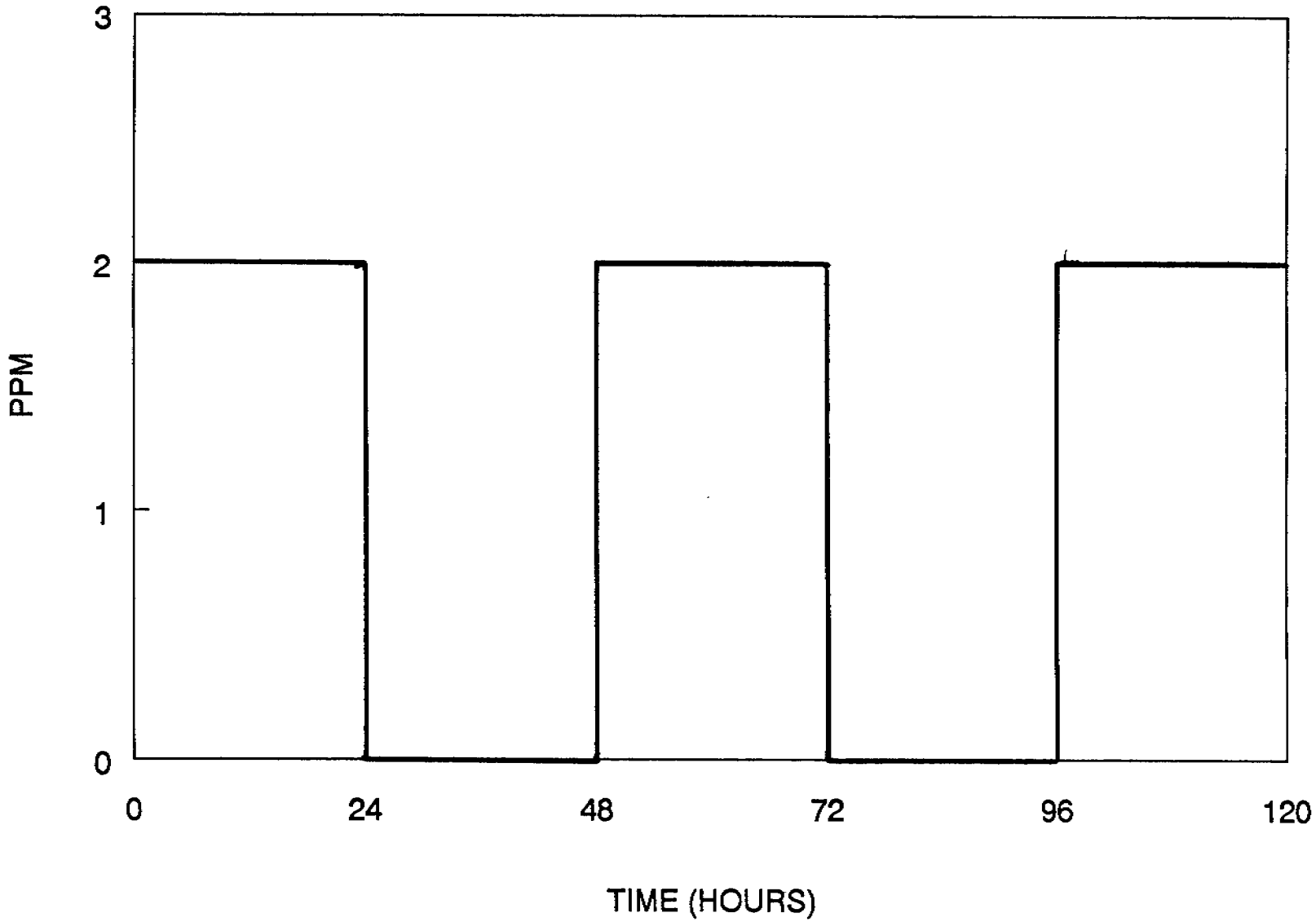
These experiments show that diffusion monitors can be used for extended sampling periods up to 1 week and still provide acceptable accuracy. When volatile compounds like acetone, isopropanol and methylene chloride are anticipated, it is essential to use the 3520 OVM which has a backup layer of sorbent.

Future work will extend to even longer sampling periods, test at high relative humidity, test at low face velocities where starvation might be a concern and investigate other sorbents which might allow thermal desorption.

2 X Coefficient of Variation + |Bias| <25%

ALTERNATING EXPOSURE

METHYLENE CHLORIDE

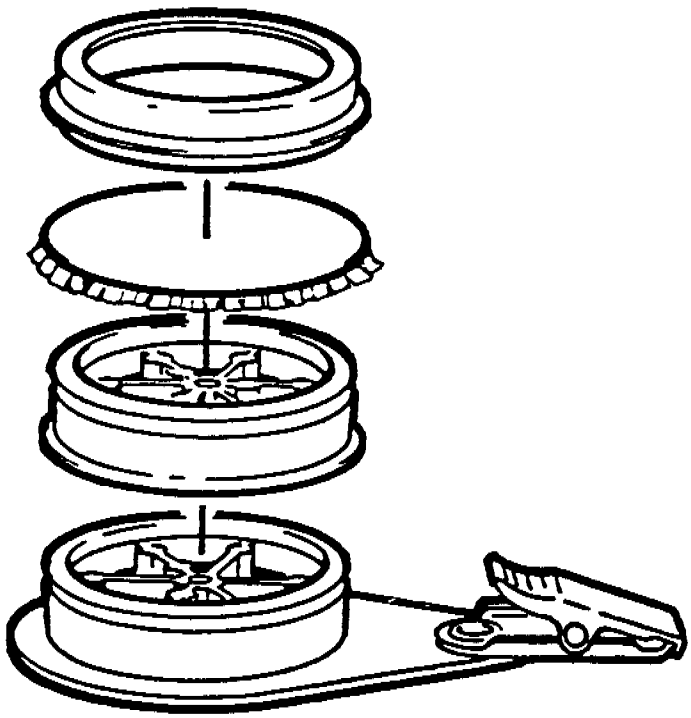


3M 110451

LONG TERM LOW LEVEL EXPOSURES
3M 3520 ORGANIC VAPOR MONITOR

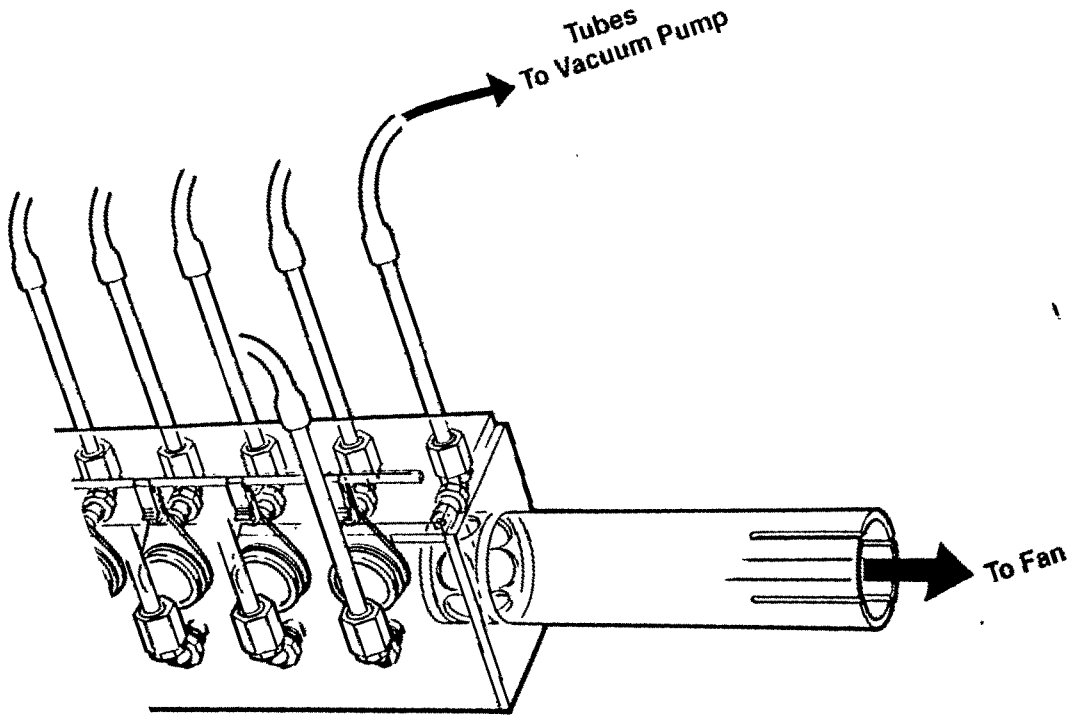
COMPOUND	EXPOSURE TIME (DAYS)	CONC (PPM)	AMOUNT FOUND (MG)	AMOUNT EXPECTED (MG)
Toluene	2 3/4	2.3	1.074	1.088
1,1,1-TCE	1	2.6	0.61	0.65
1,1,1-TCE	8	0.45	0.83	0.85
Acetone	5	2.86	1.767	1.97

COMPOUND	CV (%)	BIAS (%)	ACCURACY %
Toluene	7.4	-1.3	16.1
1,1,1-TCE	4.8	-6.2	15.8
1,1,1-TCE	5.5	-2.4	13.4
Acetone	3.6	-10.3	17.4



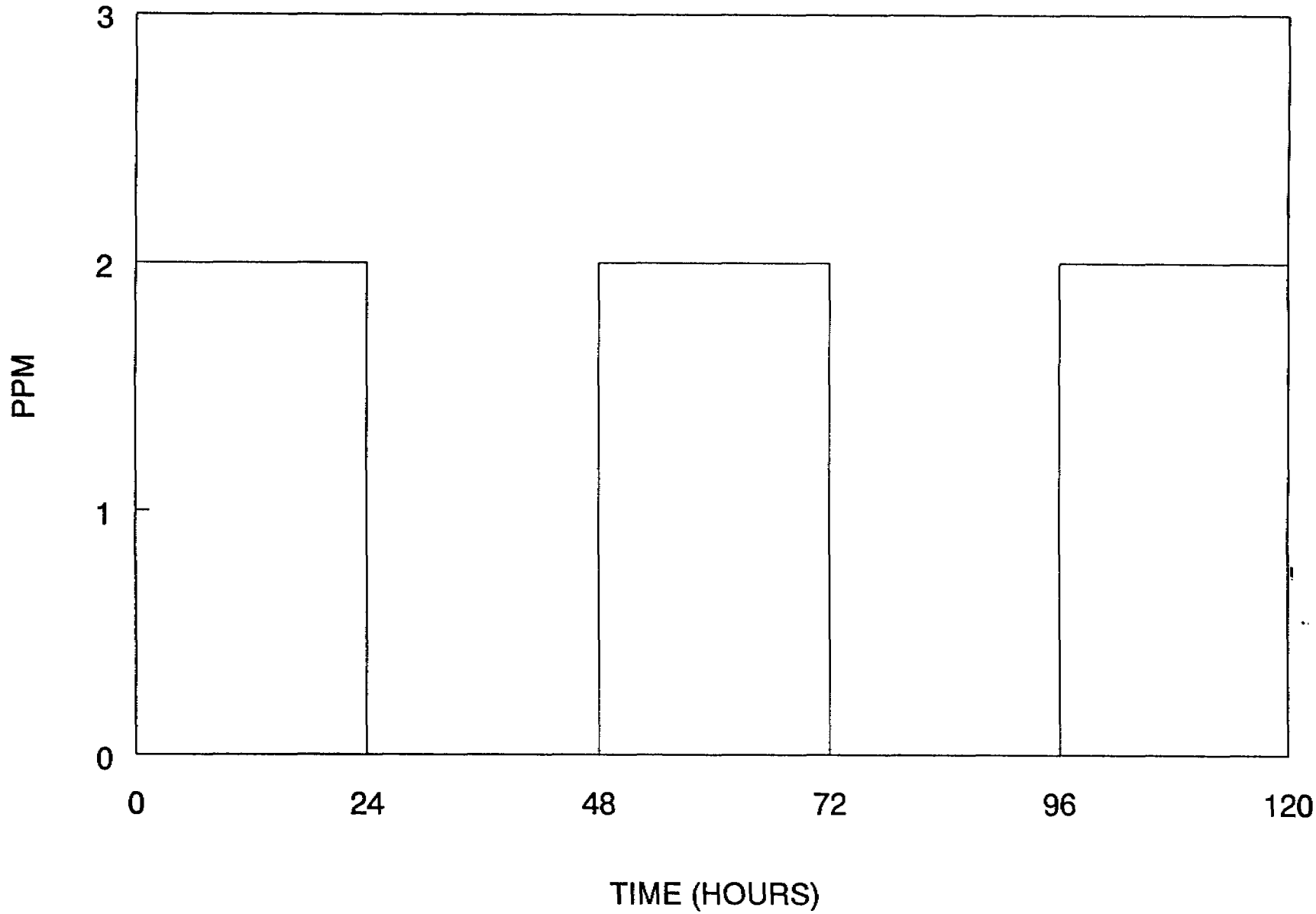
3M 110453

3M 110454


Tubes
To Vacuum Pump
To Fan

ALTERNATING EXPOSURE

METHYLENE CHLORIDE

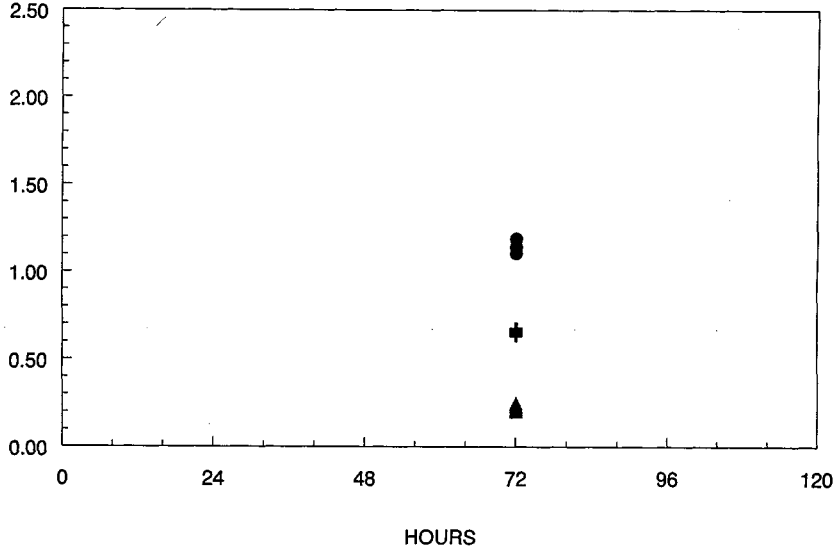


3M 110455

3M 3520 Methylene Chloride Uptake Rate

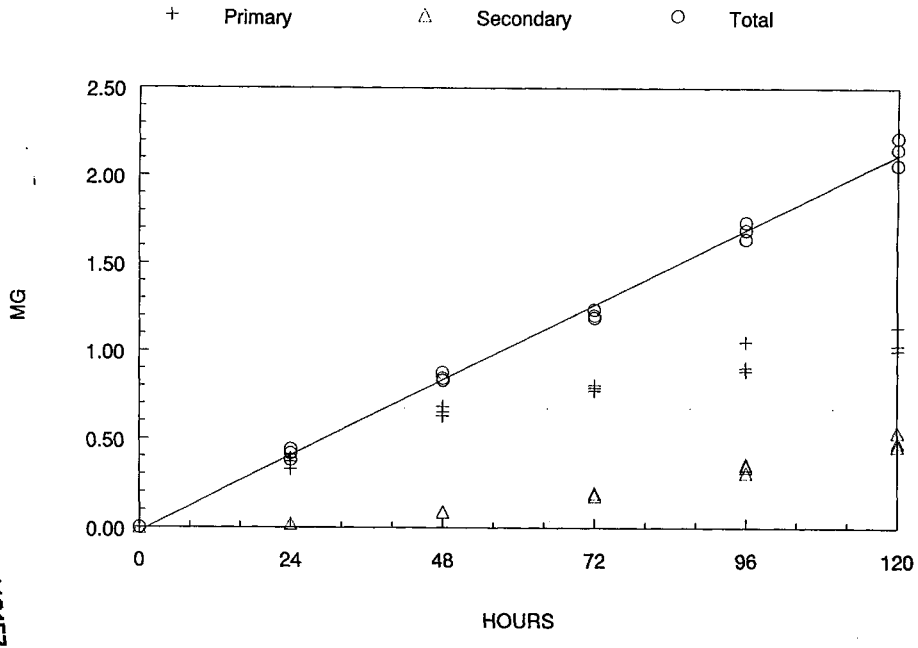
5 Days Exposure • 2 ppm & 30% RH

+ Primary ▲ Secondary ● Total



3M 3520 Methylene Chloride Uptake Rate

5 Days Exposure • 2 ppm & 30% RH



TOLUENE VALIDATION			1995						
The exposure level (1EL) was 100 ppm.									
Using our published sampling rate of 31.4 +/- .6 cc/min, an 8 hr exposure at									
1 EL = 5.68 mg, 0.5 EL = 2.84 mg and 0.1 EL = 0.57 mg.									
Desorption Efficiency									
1 1/2 mL CS2 used for desorption.				GC/FID 30M x .25mm x .25um DB5 or DBWax.					
Spike	mg	recovery	ave rec	std dev	cv	ave rec			
5.636	5.842841	1.0367	1.019875	0.012286	1.204671	1.000117			
5.636	5.676579	1.0072							
5.636	5.739139	1.0183							
5.636	5.733503	1.0173							
3.0345	3.118859	1.0278	1.01965	0.026215	2.570962				
3.0345	3.125535	1.03							
3.0345	2.977148	0.9811							
3.0345	3.15497	1.0397							
0.434	0.407439	0.9388	0.960825	0.021069	2.192753				
0.434	0.410911	0.9468							
0.434	0.424756	0.9787							
0.434	0.424886	0.979							
Storage									
Spike with 2.601 mg (.5EL) plus 40 uL H2O stored at RT and 4 C.									
mg					Recovery				
initial	2wks RT	2wks cold	3wks RT	3wks cold	initial	2wks RT	2wks cold	3wks RT	3wks cold
2.658	2.541	2.704	2.627	2.684	1.021915	0.976932	1.0396	1.009996	1.031911
2.67	2.628	2.643	2.666	2.716	1.026528	1.010381	1.016148	1.02499	1.044214
2.558	2.678	2.68	2.742	2.747	0.983468	1.029604	1.030373	1.05421	1.056132
2.644	2.651	2.719	2.756	2.668	1.016532	1.019223	1.045367	1.059592	1.025759
				average	1.012111	1.009035	1.032872	1.037197	1.039504
				std dev	0.019527	0.022798	0.012746	0.023663	0.013482
				cv	1.929361	2.259428	1.233991	2.281485	1.296918

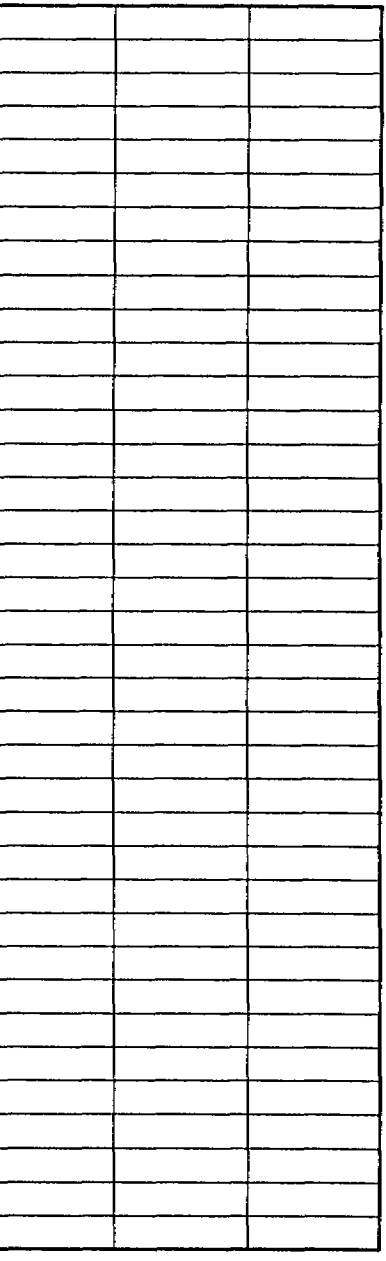
3M 110469

Humidity Effect on Uptake Linearity									
Exposure to 94.8 ppm @ 50%RH									
time min	mg	mg corr	SR	ave SR	std dev	ave mg	std dev	cv(%)	
120	1.387	1.363	31.71884	30.75074	1.120409	1.321	0.048134	3.644	
120	1.291	1.268	29.52345						
120	1.356	1.332	31.00992						
242	2.801	2.752	31.76288	30.99555	1.509278	2.685	0.130761	4.869	
242	2.58	2.535	29.25678						
242	2.819	2.770	31.967						
362	4.133	4.061	31.33134	29.69895	1.430686	3.849	0.185415	4.817	
362	3.781	3.715	28.66291						
362	3.839	3.772	29.10259						
482	5.478	5.382	31.18869	31.24752	0.247277	5.392	0.04267	0.791	
482	5.451	5.355	31.03497						
482	5.536	5.439	31.51891						
		Ave SR	30.7						
		std dev	1.2						
		cv	3.9						
Exposure to 93.9 ppm @80%RH									
time min	mg	mg corr	SR	ave SR	std dev	ave mg	std dev	cv	
130	1.453	1.441197	30.96615	30.36941	1.08941	1.413	0.050702	3.587	
130	1.366	1.354904	29.11201						
130	1.456	1.444173	31.03008						
250	2.934	2.910167	32.51509	30.78997	2.272368	2.756	0.203382	7.380	
250	2.546	2.525319	28.21521						
250	2.855	2.831809	31.6396						
370	3.778	3.747311	28.28949	29.39521	0.995823	3.894	0.13191	3.388	
370	4.036	4.003216	30.22138						
370	3.963	3.930809	29.67476						
490	5.359	5.315469	30.30069	29.6825	1.41681	5.207	0.248543	4.773	
490	5.427	5.382917	30.68518						
490	4.963	4.922686	28.06164						
		Ave SR	30.1						
		std dev	1.4						
		cv	4.7						

Average Combined SR			30.4						
Combined Std Dev			1.3						
CV			4.3						
Bias			-3.3						
Accuracy			12.0						
Exposure to 295 ppm (1111 mg/m3) @50%RH									
in .25 X 1.75 in Al chamber at 30 scfh (FV=178 fpm)									
339	13.277	13.01667	34.53892						
426	16.106	15.7902	33.34161						
657	23.953	23.48333	32.15163						
657	25.384	24.88627	34.07243						
721	27.401	26.86373	33.51503						
721	27.748	27.20392	33.93946						
		Ave SR	33.6						
		std dev	0.8						
		CV	2.5						
This experiment shows linear uptake up to 12 hours at 300 ppm.									
Only a trace was found on the backup of one of the 12 hour samples									
showing that the capacity of the 3500 OVM is at least 27 mg.									
Rev rs Diffusion									
31 min @204 ppm @80%RH (A)+ 7 1/2 hrs @ 0 ppm(B)									
mg A	mg A corr	mg B	mg B corr	SR A	SR B				
0.787	0.771569	0.777	0.761765	32.37527	31.96389				
0.899	0.881373	0.81	0.794118	36.98267	33.32143				
0.759	0.744118	0.766	0.75098	31.22341	31.51138				
0.774	0.758824	0.759	0.744118	31.84048	31.22341				
0.827	0.810784	0.787	0.771569	34.02077	32.37527				
0.715	0.70098	0.801	0.785294	29.41336	32.95119				
average	0.777941		0.767974	ave SR	32.43354				
stdev	0.062048		0.019457						
cv	7.975932		2.533541						
Difference equals -1.3 % after 7 1/2 hrs at 0 ppm.									

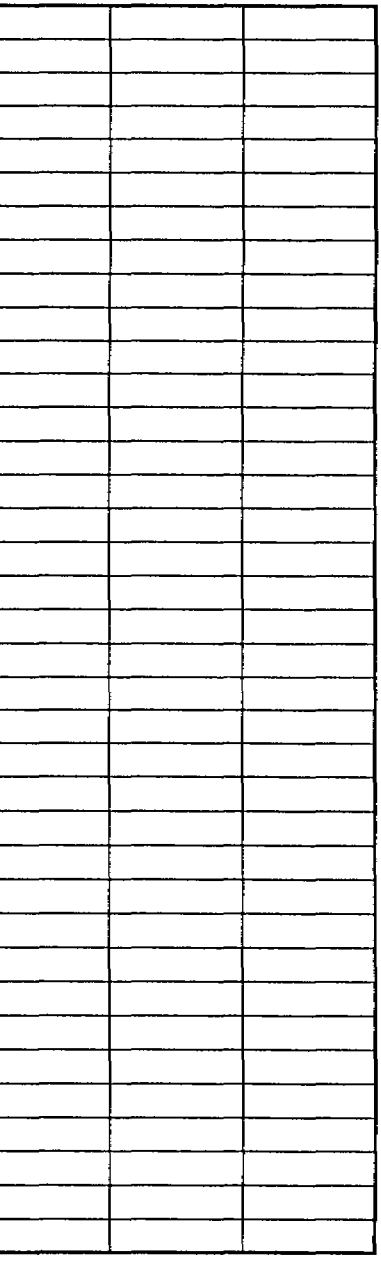
Concentration-Time									
Expose 477 min @ 186.4 ppm (2EL) @ 50%RH									
mg	mg corr	sr	ave sr	std dev	cv	bias	acc		
10.555	10.34804	30.88335	32.00155	0.785679	2.455128	1.915767	6.826023		
10.932	10.71765	31.98643							
11.058	10.84118	32.3551							
11.365	11.14216	33.25337							
10.813	10.60098	31.63825							
10.9	10.68627	31.8928							
Expose 15 and 480 min @ 11.2 ppm (.1EL) @50%RH									
0.0166	0.016275	25.70569	27.07356	1.347908	4.978687	-13.7785	23.73583		
0.0178	0.017451	27.56393							
0.0163	0.01598	25.24113							
0.0175	0.017157	27.09937							
0.0183	0.017941	28.3382							
0.0184	0.018039	28.49306							
0.609	0.597059	29.47057	29.42298	0.84738	2.879994	-6.29623	12.05622		
0.6143	0.602255	29.72704							
0.6344	0.621961	30.69972							
0.5891	0.577549	28.50757							
0.5878	0.576275	28.44466							
0.6135	0.601471	29.68833							
Exposure 15 min @ 196 ppm (2EL) @ 50%RH									
0.36145	0.354363	31.9839	31.93729	1.524634	4.773837	1.711127	11.2588		
0.38584	0.378275	34.14211							
0.33521	0.328637	29.66198							
0.35031	0.343441	30.99814							
0.37025	0.36299	32.76259							
0.36248	0.355373	32.07504							

Face Velocity-Orientation							
mean	std dev	coef var		Bias=	-2.8		
1.338	0.086	6.4		Accuracy =		15.6	
Using data from19-399 fpm.				SR =	30.50708		
Excludes 3, 10 and 14 fpm data.							
Mean corrected for rec of .97 =							
1.380							
Amount expected =		1.42					
Data corrected to 100ppm for 120 min.							
mg	mg corr	av par/per	std dev	ave	std dev	fpm	
1.435	1.435	1.330	0.131	1.316	0.101	28.8	
1.372	1.372						
1.183	1.183						
1.388	1.388	1.302	0.088				
1.307	1.307						
1.212	1.212						
1.208	1.381	1.289	0.080	1.308	0.085	19	
1.088	1.243						
1.087	1.242						
1.255	1.434	1.327	0.103				
1.153	1.318						
1.075	1.229						
1.252	1.192	1.131	0.094	1.166	0.074	9.7	
1.238	1.179						
1.074	1.023						
1.27	1.210	1.200	0.034				
1.221	1.163						
1.29	1.229						
1.119	1.079	1.157	0.090	1.211	0.086	14.2	



3M 110473

1.178	1.136						
1.302	1.256						
1.274	1.229	1.266	0.037				
1.312	1.265						
1.351	1.303						
1.259	1.201	1.271	0.076	1.310	0.067	24	
1.417	1.351						
1.324	1.263						
1.404	1.339	1.349	0.032				
1.452	1.385						
1.387	1.323						
1.244	1.208	1.196	0.111	1.272	0.117	59.5	
1.113	1.081						
1.34	1.301						
1.365	1.325	1.348	0.071				
1.47	1.427						
1.329	1.290						
1.528	1.455	1.410	0.040	1.410	0.040	399	
1.538	1.465						
1.448	1.379						
1.467	1.397						
1.441	1.372						
1.461	1.391						
1.79177	1.171	1.174	0.007137	1.145	0.05778	3	
1.80833	1.182						
1.78772	1.168						
1.74597	1.141	1.117	0.076493				
1.57744	1.031						
1.80238	1.178						
2.31486	1.346	1.382	0.040075	1.393	0.047195	340 w fan	
2.36431	1.375						
2.45103	1.425						
2.53305	1.473	1.403	0.060133				
2.35019	1.366						
2.35787	1.371						
1.17468	0.947	0.999	0.050946	0.985	0.057546	3	
1.30096	1.049						

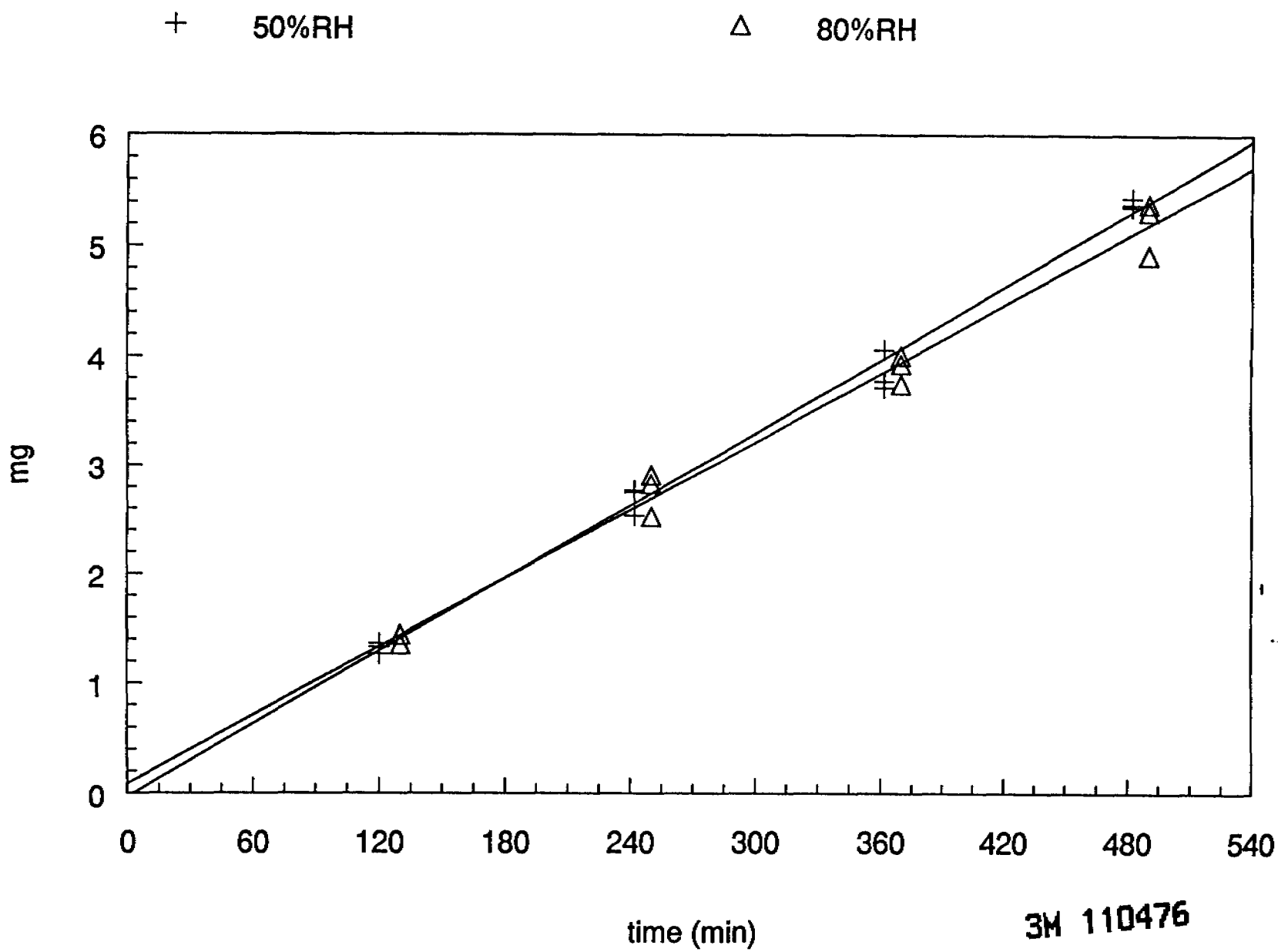


3M 110474

1.24139	1.001								
1.28218	1.034	0.970	0.070984						
1.10808	0.894								
1.2177	0.982								
1.62134	1.329	1.359	0.061718	1.359	0.048648	340 w fan			
1.60883	1.319								
1.74505	1.430								
1.59486	1.307	1.358	0.045897						
1.67304	1.371								
1.70339	1.396								
Temperature Effects									
Toluene Temperature Effect Study October, 1995									
Temp	time	Conc	mg	mg corr	SR	ave SR	sd	cv	bias
9 C	240	130	3.911	3.911	33.26319	30.09223	1.890028	6.280783	-0.21353
9 C	240	130	3.502	3.502	29.78463				
9 C	240	130	3.606	3.606	30.66915				
9 C	240	130	3.408	3.408	28.98516				
9 C	240	130	3.555	3.555	30.2354				
9 C	240	130	3.247	3.247	27.61585				
40 C	240	130	3.789	3.789	32.22557	31.46863	0.721836	2.293829	4.35064
40 C	240	130	3.743	3.743	31.83434				
40 C	240	130	3.741	3.741	31.81733				
40 C	240	130	3.685	3.685	31.34105				
40 C	240	130	3.698	3.698	31.45162				
40 C	240	130	3.544	3.544	30.14184				
RT (23 C)	244	130	3.635	3.635	30.40898	30.15662	0.400726	1.328817	
RT (23 C)	244	130	3.597	3.597	30.09109				
RT (23 C)	244	130	3.591	3.591	30.0409				
RT (23 C)	244	130	3.681	3.681	30.7938				
RT (23 C)	244	130	3.541	3.541	29.62262				
RT (23 C)	244	130	3.584	3.584	29.98234				

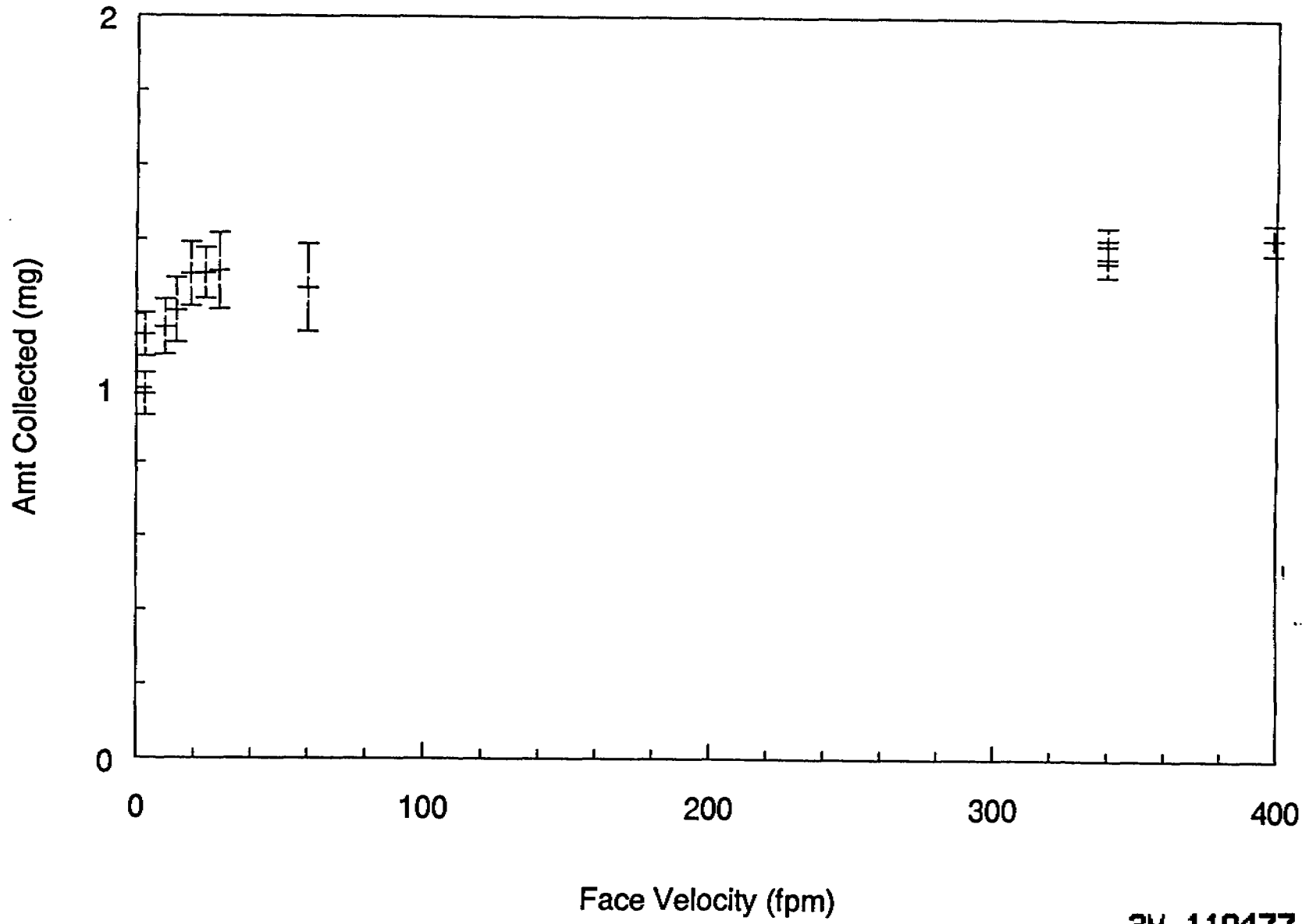
TOLUENE

95ppm•50%RH-94ppm•80%RH



Face Velocity

Toluene 100 ppm 2 hrs



3M 110477

ISOPROPANOL VALIDATION			1995					ipa2.xls			
The exposure level (1EL) was 400 ppm.											
Using our published sampling rate of 39.4 cc/min, an 8 hr exposure at											
1 EL = 18.59 mg, 0.5 EL = 9.30 mg and 0.1 EL = 1.86 mg.											
Desorption Efficiency											
1 1/2 mL acetonitrile used for desorption.				GC/FID 30M x .25mm x .25um DBWax.							
Spike	mg	recovery	ave rec	std dev	cv	ave rec					
1.96	1.887	0.962755	0.968112	0.028442	2.937889	0.955834					
1.96	1.857	0.947449									
1.96	1.867	0.952551									
1.96	1.979	1.009694									
9.42	8.972	0.952442	0.941242	0.038572	4.098006						
9.42	9.323	0.989703									
9.42	8.489	0.901168									
9.42	8.682	0.921656									
18.84	17.958	0.953185	0.958148	0.044207	4.613841						
18.84	19.257	1.022134									
18.84	17.515	0.929671									
18.84	17.476	0.927601									
Storage											
Spike with 9.42 mg (.5EL) plus 40 uL H2O stored at RT and 4 C.											
mg					Recovery						
initial	2wks RT	2wks cold	3wks RT	3wks cold	initial	2wks RT	2wks cold	3wks RT	3wks cold		
8.507	9.664	8.477	8.515	9.227	0.903079	1.025902	0.899894	0.903928	0.979512		
9.387	9.643	8.558	8.844	8.487	0.996497	1.023673	0.908493	0.938854	0.900955		
8.907	8.912	8.439	8.816	8.563	0.945541	0.946072	0.89586	0.935881	0.909023		
8.645	9.143	8.172	8.35	8.318	0.917728	0.970594	0.867516	0.886412	0.883015		
				average	0.940711	0.991561	0.892941	0.916269	0.918126		
				std dev	0.041149	0.039662	0.01775	0.025419	0.042343		
				cv	4.374277	4.000006	1.987772	2.774236	4.611846		

3M 110478

Humidity Effect on Uptake Linearity											
Exposure of 3M 3500 to 397 ppm(ave ir=400 & syr= 394.8) @ 50%RH											
time min	mg	mg corr	SR	ave SR	std dev	ave mg	std dev	cv(%)			
124	4.251	4.428	36.59418	37.19677	2.09753	4.501	0.253814	5.639			
124	4.12	4.292	35.46649								
124	4.592	4.783	39.52964								
227	8.243	8.586	38.76164	39.60806	0.803541	8.774	0.178	2.029			
227	8.583	8.941	40.36044								
227	8.443	8.795	39.70211								
358	12.456	12.975	37.13969	38.48442	3.174661	13.445	1.109089	8.249			
358	12.142	12.648	36.20344								
358	14.123	14.711	42.11013								
485	16.703	17.399	36.76168	36.16817	2.100785	17.118	0.994282	5.808			
485	15.373	16.014	33.83448								
485	17.224	17.942	37.90835								
		Ave SR	37.9								
		std dev	2.3								
		cv	6.1								
		bias	-3.9								
		acc	16.2								

Exposure of 3M 3520 to 397 ppm @ 50%RH											
time	mg A	mg B	mg A cor	mg B cor	Total	SR	ave SR	std dev	ave mg	std dev	cv(%)
124	4.251	0	4.428	0	4.428125	36.59418	37.19677	2.09753	4.501	0.253814	5.639
124	4.12	0	4.292	0	4.291667	35.46649					
124	4.592	0	4.783	0	4.783333	39.52964					
227	8.243	0	8.586	0	8.586458	38.76164	39.60806	0.803541	8.774	0.178	2.029
227	8.583	0	8.941	0	8.940625	40.36044					
227	8.443	0	8.795	0	8.794792	39.70211					
358	12.456	0.0646	12.975	0.067292	13.12304	37.56344	38.79797	3.224315	13.554	1.126436	8.311
358	12.142	0.0259	12.648	0.026979	12.70727	36.37334					
358	14.123	0.0529	14.711	0.055104	14.83269	42.45714					
485	16.703	0.1756	17.399	0.182917	17.80138	37.61194	36.98728	2.119015	17.506	1.00291	5.729
485	15.373	0.1635	16.014	0.170313	16.38823	34.62615					
485	17.224	0.1684	17.942	0.175417	18.32758	38.72374					
					Ave SR	38.1					
					std dev	2.2					
					cv	5.8					
					bias	-3.2					
					acc	14.8					

Exposure of 3M 3500 to 427 ppm (ave of ir=440 and pump = 414) @80%RH											
time min	mg	mg corr	SR	ave SR	std dev	ave mg	std dev	cv			
120	4.422	4.60625	36.5715	38.84309	2.487127	4.892	0.313258	6.403			
120	5.018	5.227083	41.50063								
120	4.65	4.84375	38.45714								
240	8.894	9.264583	36.77826	37.05945	0.36577	9.335	0.092139	0.987			
240	8.93	9.302083	36.92713								
240	9.062	9.439583	37.47297								
360	12.776	13.30833	35.22068	34.81175	1.416484	13.154	0.535226	4.069			
360	12.056	12.55833	33.23579								
360	13.051	13.59479	35.97879								
480	15.762	16.41875	32.58933	33.46598	1.967705	16.860	0.991345	5.880			
480	17.276	17.99583	35.71965								
480	15.52	16.16667	32.08897								
		Ave SR	36.0	37.95127	AveSR w/o6& 8hr 80%						
		std dev	2.6	1.866078	Uptake deviation >5% @6&8hrs						
		cv	7.3	4.917036							
		bias	-8.5	-3.7							
		acc	23.1	13.5							

Exposure of 3M 3520 to 427 ppm @ 80%RH											
time	mg A	mg B	mg A cor	mg B cor	Total	SR	ave SR	std dev	ave mg	std dev	cv(%)
120	4.422	0	4.606	0	4.60625	36.5715	38.84309	2.487127	4.892	0.313258	6.403
120	5.018	0	5.227	0	5.227083	41.50063					
120	4.65	0	4.844	0	4.84375	38.45714					
240	8.894	0.014	9.265	0.014583	9.296667	36.90562	37.21714	0.341414	9.375	0.086003	0.917
240	8.93	0.026	9.302	0.027083	9.361667	37.16366					
240	9.062	0.012	9.440	0.0125	9.467083	37.58214					
360	12.776	0.192	13.308	0.2	13.74833	36.38514	35.88524	1.563047	13.559	0.590606	4.356
360	12.056	0.148	12.558	0.154167	12.8975	34.1334					
360	13.051	0.191	13.595	0.198958	14.0325	37.13719					
480	15.762	0.652	16.419	0.679167	17.91292	35.55507	37.03216	2.37948	18.657	1.1988	6.425
480	17.276	0.892	17.996	0.929167	20.04	39.77709					
480	15.52	0.808	16.167	0.841667	18.01833	35.76431					
					Ave SR	37.2					
					std dev	2.0					
					cv	5.3					
					bias	-5.5					
					acc	16.0					
Ave Combined SR		3M 3500	37.0	37.89333	3M 3520	37.7		Non-linear difference >5%			
Combined Std Dev			2.6	2.124904		2.1					
CV			7.0	5.607594		5.6		8hr 80%	7.155172		
Bias			-6.2	-3.8		-4.3		6hr 80%	5.671387		
Accuracy			20.2	15.0		15.5					
			all points	w/o nonlinear pts							

Reverse Diffusion											
30 min @2EL = 800 (ave ir=818 & syr= 772) ppm @80%RH (A)+ 7 1/2 hrs @ 0 ppm(B)											
mg A	mg A corr	mg B	mg B corr	mg back	mg bk cor	tot	SR A	SR B	SR TOT		
2.194	2.285417	2.19	2.28125	0.018	0.01875	2.3225	38.7399	38.66928	39.3685		
2.17	2.260417	2.014	2.097917	0.011	0.011458	2.123125	38.31613	35.56161	35.98891		
2.113	2.201042	2.067	2.153125	0.009	0.009375	2.17375	37.30967	36.49744	36.84705		
2.106	2.19375	1.95	2.03125	0.01	0.010417	2.054167	37.18607	34.43155	34.82		
2.16	2.25	2.093	2.180208	0.012	0.0125	2.207708	38.13956	36.95653	37.42268		
2.133	2.221875	1.977	2.059375	0.012	0.0125	2.086875	37.66281	34.90829	35.37444		
average	2.235417		2.133854			2.161354	37.89236	36.17078	36.63693		
stdev	0.035885		0.091227			0.096714					
cv	1.605311		4.275224			4.474701					
3M 3500 % Differenc		-4.54334									
3M 3520 % Differenc		-3.31314									

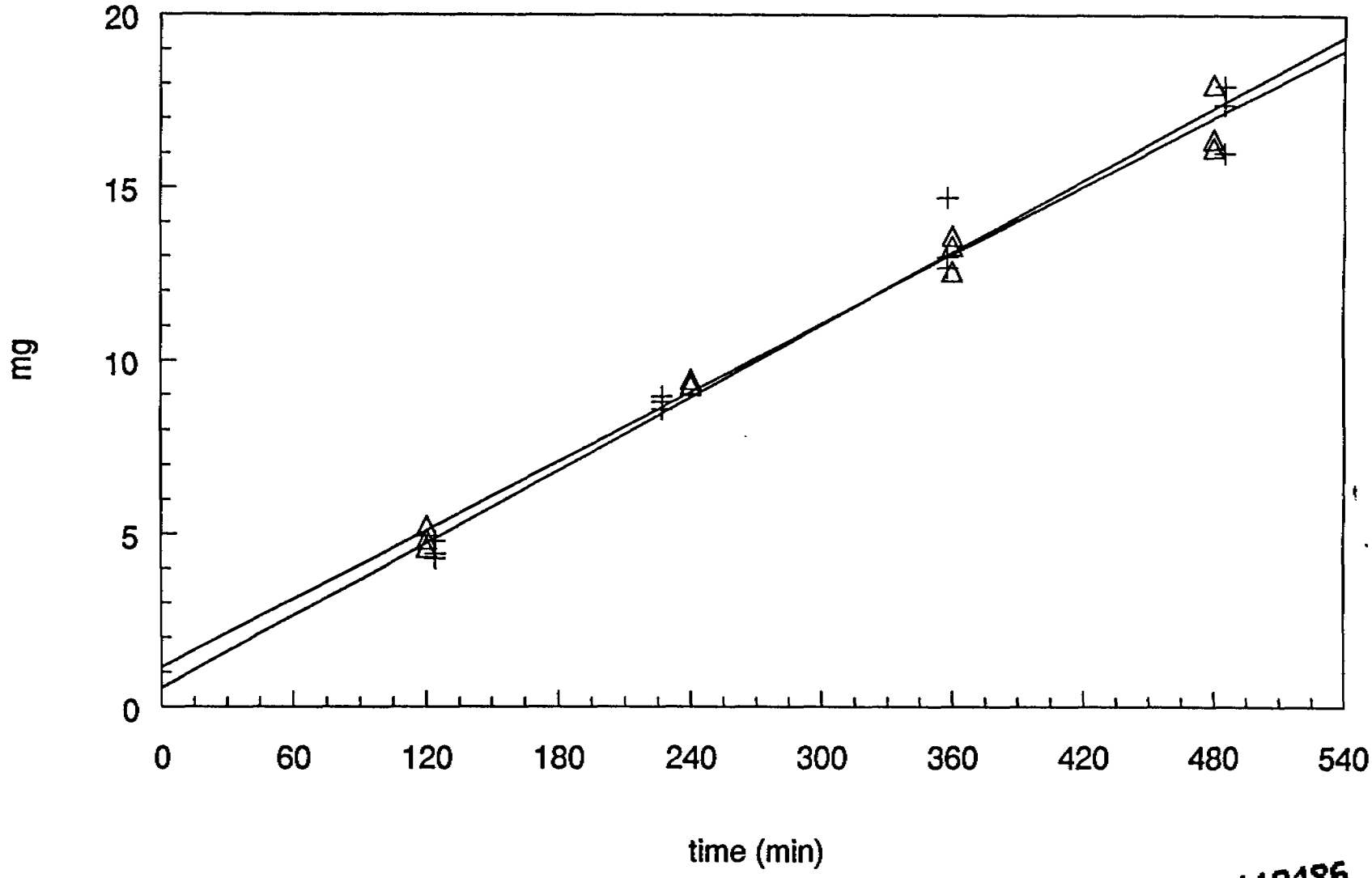
Concentration-Time											
Expose 15 min @(ir=775 pump=752.8) 764 ppm (2EL) @ 50%RH											
mg	mg corr	sr	ave sr	std dev	cv	bias	acc				
1.183	1.232292	43.74549	41.16933	2.924306	7.103119	4.490674	18.69691				
1.03	1.072917	38.08779									
1.001	1.042708	37.01541									
1.161	1.209375	42.93196									
1.125	1.171875	41.60074									
1.18	1.229167	43.63455									
Expose 16 and 480 min @ (ir=35 pump=53.2) 53.2 ppm (.1EL) @50%RH											
0.0815	0.084896	40.57506	40.12699	1.709023	4.259036	1.845153	10.36322				
0.0835	0.086979	41.57077									
0.0814	0.084792	40.52527									
0.0742	0.077292	36.94073									
0.0833	0.086771	41.47119									
0.0797	0.083021	39.67892									
2.412	2.5125	40.02742	39.45489	1.275591	3.233038	0.13931	6.605385				
2.355	2.453125	39.0815									
2.376	2.475	39.43									
2.353	2.451042	39.04831									
2.268	2.3625	37.63772									
2.501	2.605208	41.50438									

Exposure 480 min @(ir=791 pump=749.8)770 ppm (2EL) @ 50%RH (3500)											
30.67	31.94792	35.16535	33.67003	1.008734	2.99594	-14.5431	20.53495				
28.034	29.20208	32.14299									
29.404	30.62917	33.71379									
29.061	30.27188	33.32052									
29.154	30.36875	33.42715									
29.872	31.11667	34.25039									
Exposure 480 min @ 749.8 ppm (2EL) @ 50%RH (3520)											
30.67	2.13	31.94792	2.21875	36.82917	40.53819	39.14419	1.203505	3.074544	-0.64928	6.798365	
28.034	2.148	29.20208	2.2375	34.12458	37.56123						
29.404	2.56	30.62917	2.666667	36.49583	40.17128						
29.061	1.801	30.27188	1.876042	34.39917	37.86346						
29.154	2.353	30.36875	2.451042	35.76104	39.36249						
29.872	2.029	31.11667	2.113542	35.76646	39.36845						
Temperature Effects											
No specific data. Data for toluene, 1,1,1-trichloroethane , methylene chloride and hexane show											
that temperature effects are not significant (<10%) in the range 10-40C.											
Face Velocity & Orientation											
Extensive tests with toluene, hexane and 1,1,1-trichloroethane have shown that the 3M											
organic vapor monitor is not affected by orientation and face velocity as long as a minimum face											
velocity of 25 fpm is maintained.											

Isopropanol

397 ppm • 50%RH - 427 ppm • 80%RH

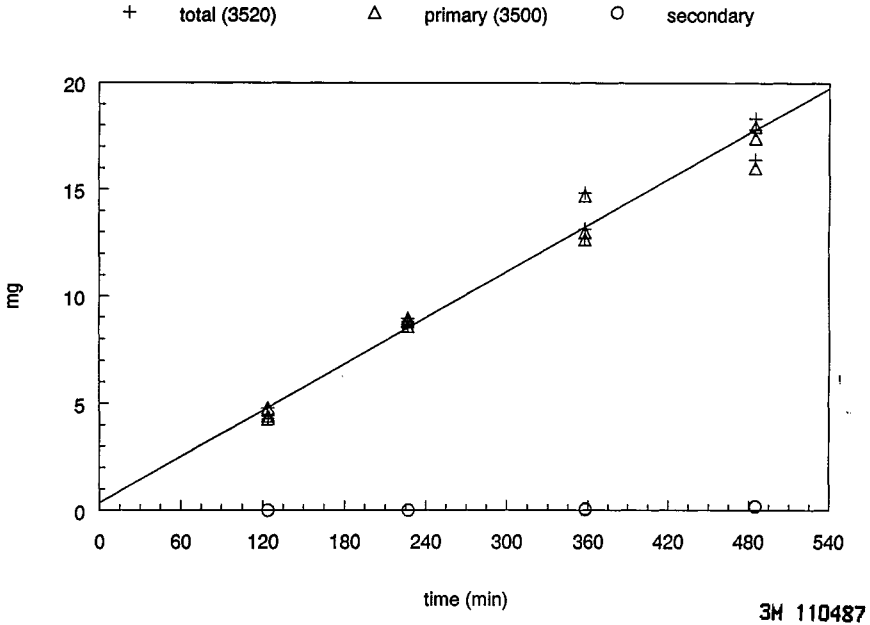
+ 50%RH △ 80%RH



3M 110486

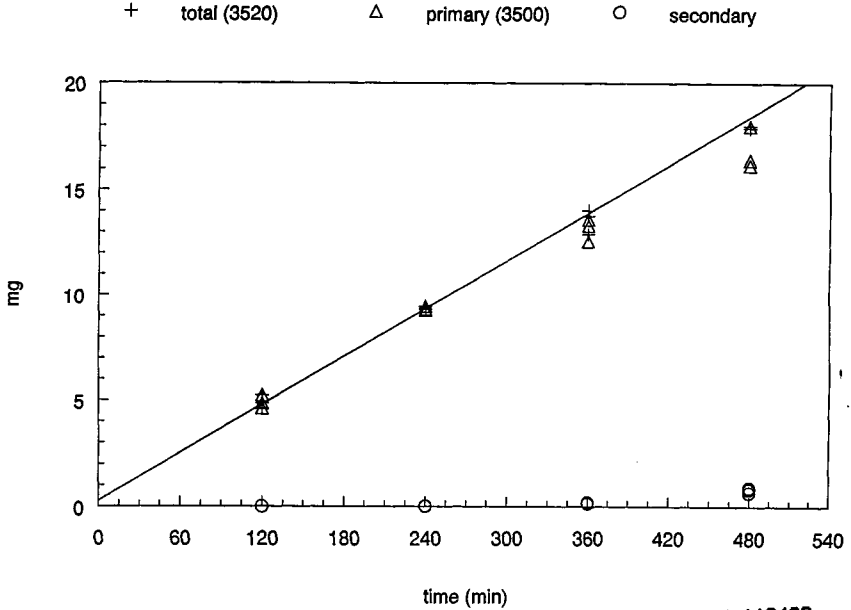
Isopropanol

397 ppm • 50%RH



Isopropanol

427 ppm • 80%RH



3M 110488

Methylene Chloride Validation				1995							
The exposure level (1 EL) was 25 ppm.											
Using our published sampling rate of 37.9 cc/min, an 8 hr exposure at 1 EL = 1.58 mg,											
0.5 EL = .791 mg and 0.1 EL = .158 mg.											
Desorption Efficiency											
1 1/2 mL CS2 used for desorption.				GC/FID 30M x .25 mm x .25 um DBWax.							
Spike	mg	recovery	ave rec	std dev	cv	Recovery					
0.159	0.136	0.855346	0.877358	0.031863	3.631705	0.87					
0.159	0.137	0.861635									
0.159	0.138	0.867925									
0.159	0.147	0.924528									
0.795	0.669	0.841509	0.871069	0.020985	2.409144						
0.795	0.693	0.871698									
0.795	0.701	0.881761									
0.795	0.707	0.889308									
1.590	1.403	0.88239	0.860849	0.014699	1.707543						
1.590	1.356	0.85283									
1.590	1.364	0.857862									
1.590	1.352	0.850314									
Storage											
.795 mg plus 40 uL H2O stored at RT and 4 C											
	Initial	2wks RT	2wks cold	rec Initial	rec 2 wks	rec 2wks cold					
0.795	0.713	0.738	0.747	0.896855	0.928302	0.939623					
0.795	0.73	0.775	0.784	0.918239	0.974843	0.986164					
0.795	0.822	0.736	0.761	1.033962	0.925786	0.957233					
0.795	0.721	0.747	0.768	0.906918	0.939623	0.966038					
			AVE	0.94	0.94	0.96					
			stdev	0.06	0.02	0.02					

		8wks RT	8wks cold		rec 8wks	rec 8wks cold					
0.795		0.689	0.724		0.866667	0.910692					
0.795		0.699	0.702		0.879245	0.883019					
0.795		0.716	0.69		0.900629	0.867925					
0.795		0.689	0.697		0.866667	0.87673					
			AVE		0.88	0.88					
			stdev		0.02	0.02					
Humidity Effect on Uptake Linearity											
Methylene Chloride Exposure at 24 ppm, 80 % RH, 23.5 C, 29 fpm, DE=.87											
time	mg A	mg B	mg A corr	mg B corr	mg total	mean	stdev	SR	ave SR	std dev	CV(%)
120	0.33	0	0.379	0.000	0.379	0.369	0.016932	37.91578	36.88	1.692528	4.589072
120	0.304	0	0.349	0.000	0.349			34.92847			
120	0.329	0	0.378	0.000	0.378			37.80088			
242	0.569	0.032	0.654	0.037	0.735	0.744	0.008817	36.42877	36.89595	0.437027	1.184485
242	0.563	0.039	0.647	0.045	0.746			36.96432			
242	0.571	0.038	0.656	0.044	0.752			37.29477			
361	0.678	0.125	0.779	0.144	1.095	1.094	0.047835	36.39762	36.34669	1.589427	4.372962
361	0.733	0.118	0.843	0.136	1.141			37.91005			
361	0.674	0.107	0.775	0.123	1.045			34.73242			
480	0.668	0.218	0.768	0.251	1.319	1.337	0.03528	32.96375	33.40227	0.881643	2.639472
480	0.723	0.216	0.831	0.248	1.377			34.41718			
480	0.694	0.204	0.798	0.234	1.314			32.82587			
AVE SR	stdev	cv	Bias	OSHA							
35.9	1.9	5.2	-5.3	15.7							
36.7	1.2	3.3	-3.1	9.7	w/o 8hr 80%						

Methylene Chloride Exposure at 24 ppm, 50 % RH, 22.5 C, 29 fpm, DE=.87											
time	mg A	mg B	mg A corr	mg B corr	mg total	mean	stdev	SR	ave SR	std dev	CV(%)
120	0.352	0	0.405	0.000	0.405	0.388	0.020891	40.44	38.76	2.088249	5.387868
120	0.343	0	0.394	0.000	0.394			39.41			
120	0.317	0	0.364	0.000	0.364			36.42			
240	0.673	0	0.774	0.000	0.774	0.747	0.035592	38.66	37.36	1.778865	4.761848
240	0.643	0.009	0.739	0.010	0.762			38.08			
240	0.615	0	0.707	0.000	0.707			35.33			
360	0.883	0.027	1.015	0.031	1.083	1.141	0.050318	36.09	38.01	1.676582	4.410572
360	0.966	0.026	1.110	0.030	1.176			39.19			
360	0.946	0.03	1.087	0.034	1.163			38.76			
480	1.294	0.054	1.487	0.062	1.624	1.578	0.043211	40.58	39.44	1.079842	2.737665
480	1.228	0.05	1.411	0.057	1.538			38.43			
480	1.25	0.054	1.437	0.062	1.573			39.32			
AVE SR	stdev	cv	bias	OSHA							
38.4	1.7	4.3	1.3	10.0							
Combined SR, etc. for 50% and 80%RH without 80%RH 8hr data.											
37.7	1.7	4.5	-0.6	9.5							

R verse Diffusion											
					mean	std dev	cv(%)	%diff			
30 min @ 52 ppm plus 3 1/2 hrs and 7 1/2 hrs @ 0 ppm @ 80%RH											
0.19	0	0.208791	0	0.208791	0.204396	0.009299	4.549289				
0.193	0	0.212088	0	0.212088							
0.17	0	0.186813	0	0.186813							
0.192	0	0.210989	0	0.210989							
0.186	0	0.204396	0	0.204396							
0.185	0	0.203297	0	0.203297							
0.151	0.013	0.165934	0.014286	0.197363	0.194872	0.009062	4.650484	-4.6595			
0.157	0.012	0.172527	0.013187	0.201538							
0.142	0.011	0.156044	0.012088	0.182637							
0.145	0.012	0.159341	0.013187	0.188352							
0.146	0.013	0.16044	0.014286	0.191868							
0.158	0.014	0.173626	0.015385	0.207473							
0.089	0.034	0.097802	0.037363	0.18	0.184359	0.005001	2.712635	-9.80287			
0.093	0.036	0.102198	0.03956	0.189231							
0.084	0.035	0.092308	0.038462	0.176923							
0.093	0.036	0.102198	0.03956	0.189231							
0.091	0.035	0.1	0.038462	0.184615							
0.088	0.037	0.096703	0.040659	0.186154							

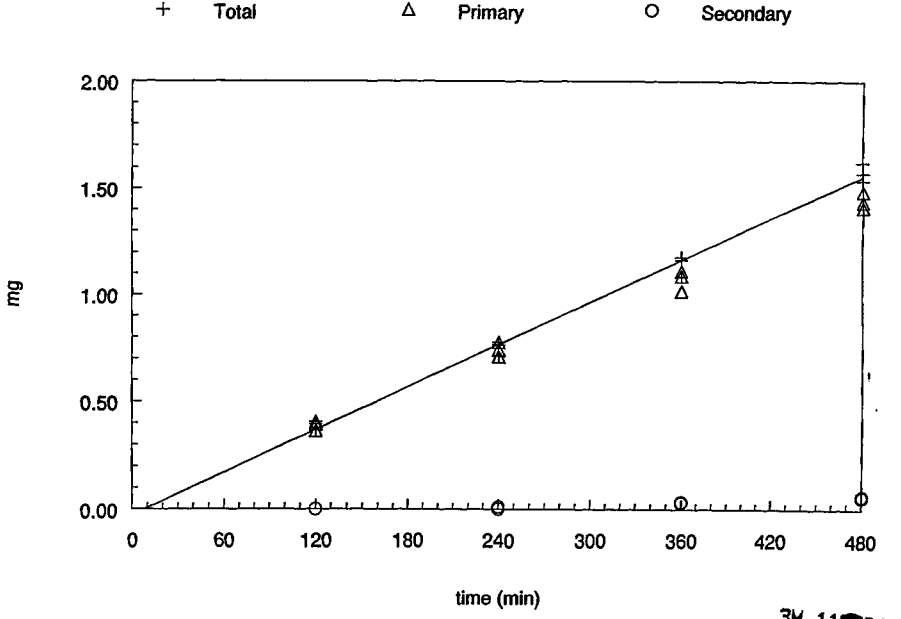
Concentration-Time											
Exposure @ 52.1 ppm (2EL) and 50%RH											
time (min)	mg	mg corr	SR	ave SR	sd	cv	bias	acc			
15	0.08498	0.102386	37.71615	38.26945	2.559761	6.688783	0.974812	14.35238			
	0.08193	0.098711	36.36249								
	0.08454	0.101855	37.52087								
	0.08037	0.096831	35.67013								
	0.08934	0.107639	39.65123								
	0.0962	0.115904	42.69586								
Exposure @4 ppm (.1EL) 50%RH											
							ave sr	std dev	cv	bias	acc
493	0.23917	0.01132	0.288157	0.013639	0.318161	46.44708	45.24155	1.631583	3.606382	19.37084	26.58361
	0.22199	0.01097	0.267458	0.013217	0.296535	43.28991					
	0.24709	0.01047	0.297699	0.012614	0.325451	47.51119					
	0.23749	0.01046	0.286133	0.012602	0.313858	45.81881					
	0.22612	0.01033	0.272434	0.012446	0.299814	43.76868					
	0.22989	0.0108	0.276976	0.013012	0.305602	44.61363					
Exposure at 51 PPM (177.3 MG/M3)(2EL) @58%RH FOR 461 MIN DE=.87											
461	2.215	0.186	2.545977	0.213793	3.016322	36.90354	36.87026	0.912462	2.474792	-2.717	7.666584
	2.214	0.185	2.544828	0.212644	3.012644	36.85854					
	2.168	0.181	2.491954	0.208046	2.949655	36.0879					
	2.339	0.185	2.688506	0.212644	3.156322	38.61639					
	2.156	0.193	2.478161	0.221839	2.966207	36.2904					
	2.219	0.17	2.550575	0.195402	2.98046	36.46478					

Exposure for 16 min at 9.1 ppm (.4EL) @50%RH											
14:1 SPLIT DE = .97											
amount collected		amount corrected			SR						
0.020863		0.021508			42.5259						
0.019654		0.020262			40.06244						
0.020362		0.020992			41.50567						
0.02129		0.021948			43.39681						
0.020045		0.020665			40.85871						
0.019093		0.019683			38.91781						
		0.020843		AVE SR	41.2112						
				STD DEV	1.630679						
				CV	3.956884						
				bias	8.736675						
				ACCUR	16.65044						
Orientation-Face Velocity Effects											
Extensive tests with toluene, hexane and 1,1,1-trichloroethane have shown that the 3M											
organic vapor monitor is not affected by orientation and face velocity as long as a minimum face											
velocity of 25 fpm is maintained.											
T mperature Effects											
Exposed to 20 ppm for 243 min @RT											
mg	mg corr	SR	ave SR	ave mg							
0.7816	0.898391	53.21656	52.71045	0.889847							
0.795	0.913793	54.12892									
0.7536	0.866207	51.31013									
0.7631	0.877126	51.95695									
0.7903	0.908391	53.80891									
0.7614	0.875172	51.84121									

Exposed to 22.5 ppm for 243 min @40 C							
mg	mg corr	SR	ave SR	ave mg			
0.9539	1.096437	57.73146	56.87508	0.960153	7.900969		
0.909	1.044828	55.01404					
0.9567	1.099655	57.90092					
0.9482	1.089885	57.38649					
0.9328	1.072184	56.45446					
0.9379	1.078046	56.76312					
Exposed to 21.1 ppm for 243 min @ 11.6 C							
mg	mg corr	SR	ave SR	ave mg	%diff		
0.8604	0.988966	55.52776	54.12623	0.913748	2.685964		
0.8396	0.965057	54.18539					
0.8225	0.945402	53.0818					
0.8375	0.962644	54.04986					
0.8263	0.94977	53.32704					
0.8458	0.972184	54.58552					

Methylene Chloride Uptake Rate

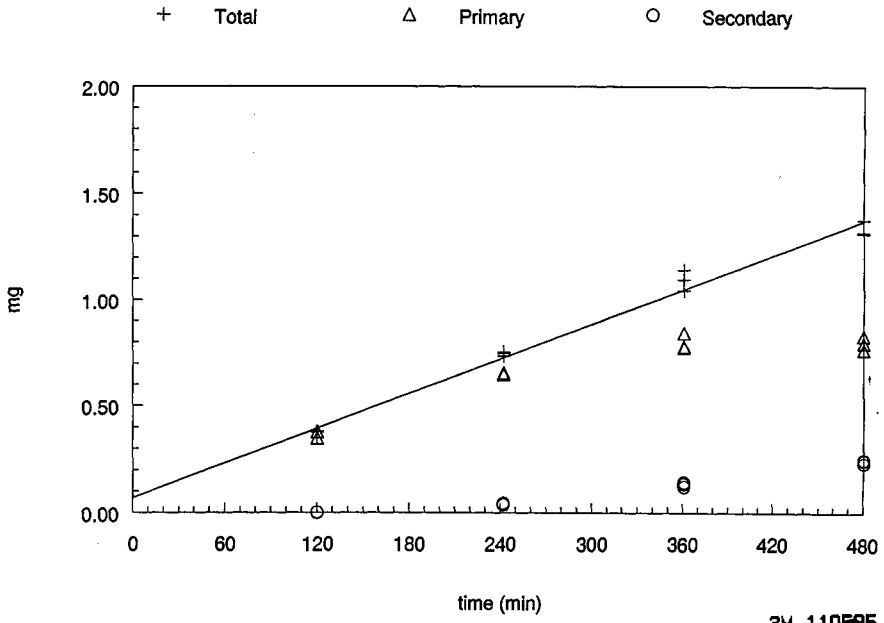
24 ppm, 50% RH, 23 C, 29 fpm



3M 11[illegible]04

Methylene Chloride Uptake Rate

24 ppm, 80% RH, 23 C, 29 fpm



3M 110[illegible]

1,1,1-Trichloroethane Validation				1995					tce3.xls			
The exposure level (1 EL) is 350 ppm.												
Using our published sampling rate of 30.9 +/- .3 cc/min, an 8 hr exposure at												
1 EL = 28.3 mg, 0.5 EL = 14.2 mg and 0.1 EL = 2.83 mg.												
Desorption Efficiency												
1 1/2 mL CS2 used for desorption.				GC/FID 30Mx.25mmx.25um DB5.								
Spike	mg	recovery	ave rec	std dev	Recovery							
28.1	27.769	0.988	0.988	0.003	1.00							
28.1	27.858	0.991										
28.1	27.737	0.987										
28.1	27.684	0.985										
13.38	13.250	0.990	0.988	0.009								
13.38	13.205	0.987										
13.38	13.070	0.977										
13.38	13.357	0.998										
2.676	2.762	1.032	1.027	0.008								
2.676	2.740	1.024										
2.676	2.772	1.036										
2.676	2.723	1.018										
Storage												
Spike w 13.38 mg (0.5 EL) plus 40 uL H2O stored at RT and 4 C.												
mg					Recovery							
initial	2wks RT	2wks cold	3wks RT	3wks cold	initial	2wks RT	2wks cold	3wks RT	3wks cold			
13.637	12.614	13.046	13.474	13.948	1.02	0.94	0.98	1.01	1.04			
13.566	12.588	13.238	13.378	13.437	1.01	0.94	0.99	1.00	1.00			
13.429	13.105	13.241	13.459	13.618	1.00	0.98	0.99	1.01	1.02			
13.767	12.906	13.145	13.399	13.464	1.03	0.96	0.98	1.00	1.01			
				average	1.02	0.96	0.98	1.00	1.02			
				std dev	0.01	0.02	0.01	0.00	0.02			
				cv	1.04	1.93	0.70	0.34	1.72			

Humidity Effect on Uptake Linearity												
Exposure to 367 ppm @ 50%RH (3520 in G, 3500 in K)												
time min	mg A	mg B	A corr	B corr	mg tot	3520 SR	Ave SR	AVE MG	std dev sr	3500 SR	ave sr	stdev sr
110	7.041	0	6.835922	0	6.835922	31.03336	31.43592	6.924595	0.374441	31.03336	31.43592	0.374441
110	7.209	0	6.999029	0	6.999029	31.77383				31.77383		
110	7.147	0	6.938835	0	6.938835	31.50056				31.50056		
235	15.24	0	14.79612	0	14.79612	31.44158	31.13349	14.65113	0.267323	31.44158	31.13349	0.267323
235	15.008	0	14.57087	0	14.57087	30.96294				30.96294		
235	15.024	0	14.58641	0	14.58641	30.99595				30.99595		
351	22.046	0.007	21.40388	0.006796	21.41883	30.47285	29.84447	20.97715	0.54421	30.45158	29.81205	0.553871
351	21.348	0.013	20.72621	0.012621	20.75398	29.52696				29.48745		
351	21.355	0.012	20.73301	0.01165	20.75864	29.53359				29.49712		
470	29.003	0.045	28.15825	0.043689	28.25437	30.0201	29.30503	27.58136	0.738922	29.91798	29.19761	0.74711
470	27.557	0.052	26.75437	0.050485	26.86544	28.54437				28.42636		
470	28.354	0.045	27.52816	0.043689	27.62427	29.35063				29.2485		
					ave SR	30.42973				30.39477		
					std dev	1.02039				1.060039		
					cv	3.353268				3.487571		

Exposure to 369 ppm @ 80%RH												
time min	mg A	mg B	A corr	B corr	mg tot	3520 SR	Ave SR	ave mg	stdev sr	3500 SR	ave sr	stdev sr
115	7.006	0	6.801942	0	6.801942	29.37644	29.7622	6.891262	1.256996	29.53653	29.92439	1.263846
115	7.433	0	7.216505	0	7.216505	31.16687				31.33672		
115	6.855	0	6.65534	0	6.65534	28.74329				28.89993		
230	13.822	0.122	13.41942	0.118447	13.68	29.54081	27.73361	12.84311	1.834187	29.13602	27.65132	1.609792
230	13.225	0.013	12.83981	0.012621	12.86757	27.78644				27.87758		
230	12.306	0.016	11.94757	0.015534	11.98175	25.87358				25.94038		
333	18.811	0.344	18.26311	0.333981	18.99786	28.33509	27.99027	18.76667	1.182293	27.38765	26.97902	1.06648
333	19.081	0.418	18.52524	0.405825	19.41806	28.96181				27.78076		
333	17.699	0.328	17.1835	0.318447	17.88408	26.67389				25.76865		
469	23.765	1.391	23.07282	1.350485	26.04388	27.58017	27.26152	25.74298	0.312156	24.567	24.23069	0.448557
469	22.947	1.616	22.27864	1.568932	25.73029	27.24808				23.7214		
469	23.607	1.187	22.91942	1.152427	25.45476	26.9563				24.40367		
					Ave SR	28.1869			27.19636	28.18491		
					std dev	1.465519			2.345778	1.765867		
					CV	5.199292			8.625339	6.26529		
									w 8 hr	w/o 8hr		
			3M 3500	3M 3520	3M 3500							
Mean of 50% & 80%RH SRs			29.4	29.60071	28.8		Non-linear difference >5%					
Std Dev			1.76666	1.684456	2.41615							
CV			5.999315	5.690593	8.390701		8hr 80%	10.90465				
Bias			-4.70004	-4.20482	-6.81048							
OSHA Accuracy			16.69867	15.586	23.59188							
			w/o n-l pt	all pts	all pts							

Reverse Diffusion												
30 min @694 ppm @80%RH (A)+ 7 1/2 hrs @ 0 ppm(B)												
mg A		mg B		SR A	SR B	ave sr						
3.518		3.243		30.96746	28.54675							
3.827		3.497		33.68746	30.78261							
3.528		3.325		31.05549	29.26856							
3.421		3.444		30.11361	30.31607							
3.385		3.407		29.79672	29.99037							
3.774		3.528		33.22092	31.05549							
average	3.5755		3.407333									
stdev	0.183509		0.107452									
cv	5.132397		3.153542									
%diff			4.703305									
ave sr				31.47361	29.99331	30.73346						
Concentration-Time												
Expose 480 min @37.8 ppm (.1EL) @ 50%RH												
mg	mg corr	SR	ave SR	std dev	cv	bias	acc					
3.209	3.209	32.41359	31.00284	0.74748	2.411006	0.33282	5.154831					
3.022	3.022	30.52473										
3.085	3.085	31.16109										
3.028	3.028	30.58534										
3.063	3.063	30.93887										
3.009	3.009	30.39342										
Expose 17 min @36.7 ppm (.1EL) @ 50%RH												
mg	mg corr	SR	ave SR	std dev	cv	bias	acc					
0.115	0.115	33.78106	32.89982	1.050946	3.194383	6.471908	12.86067					
0.114	0.114	33.48732										
0.113	0.113	33.19357										
0.108	0.108	31.72483										
0.107	0.107	31.43108										
0.115	0.115	33.78106										

Expose 15 min @ 701 ppm (2EL) @ 50%RH												
mg	mg corr	SR	ave SR	std dev	cv	bias	acc					
1.862	1.862	32.45345	32.70327	1.147199	3.507903	5.835829	12.85164					
1.944	1.944	33.88266										
1.87	1.87	32.59289										
1.886	1.886	32.87175										
1.761	1.761	30.69309										
1.935	1.935	33.72579										
Expose 3500s to 480 min @695 ppm (2EL) @50%RH												
mg	mg corr	SR	ave SR	std dev	cv	bias	acc					
51.663	51.663	28.38207	29.32552	1.680546	5.73066	-5.09541	16.55672					
50.727	50.727	27.86786										
54.985	54.985	30.20707										
49.892	49.892	27.40914										
57.625	57.625	31.65741										
55.39	55.39	30.42957										
Expose 3520s to 480 min @695 ppm (2EL) @50%RH												
mg A	mg B	tot mg cor	SR	ave SR	std dev	cv	bias	acc				
51.663	0.836	53.5022	29.39247	30.35586	1.917036	6.315208	-1.76096	14.39138				
50.727	0.57	51.981	28.55677									
54.985	0.864	56.8858	31.25132									
49.892	0.622	51.2604	28.16089									
57.625	0.945	59.704	32.79955									
55.39	1.278	58.2016	31.97418									

Temperature Effects												
120 min exposures												
temp	ppm	mg	ave mg	% diff								
RT	238	5.508	5.4625									
		5.442										
		5.394										
		5.14										
		5.372										
		5.919										
42 C	237	5.448	5.393333	-1.26621								
		4.98										
		4.957										
		5.772										
		5.435										
		5.768										
12 C	239	5.734	5.887	7.771167								
		5.92										
		5.821										
		5.884										
		5.915										
		6.048										

Face Vel city-Orientation												
1,1,1-Trichloroethane Face Velocity and Orientation Test (June-July, 1994)												
Using data from 14-400fpm												
Excludes 3 and 10 fpm												
Mean	2.152359											
Std dev	0.172512											
Coef Var	8.015002											
Amt expec	2.225573											
Bias	-3.28969											
Acc	19.31969											
Data Normalized to 120 min at 110 ppm												
mg	mg corr	av par/per	stdev	ave	stdev	fpm						
2.15369	2.194	2.212	0.088988	2.226	0.105537	28						
2.09523	2.134											
2.26707	2.309											
2.14874	2.189	2.24	0.139162									
2.35343	2.397											
2.0943	2.133											
2.11722	2.025	2.131	0.128851	2.113	0.144662	24						
2.1887	2.094											
2.37792	2.275											
2.02467	1.937	2.095	0.186392									
2.1412	2.048											
2.40501	2.3											
2.37608	2.273	2.248	0.186401	2.177	0.201666	19						
2.53035	2.42											
2.14325	2.05											
1.94741	1.863	2.105	0.227411									
2.41886	2.314											
2.23674	2.139											
1.96915	2.111	2.149	0.033216	2.161	0.092121	14						
2.01674	2.162											

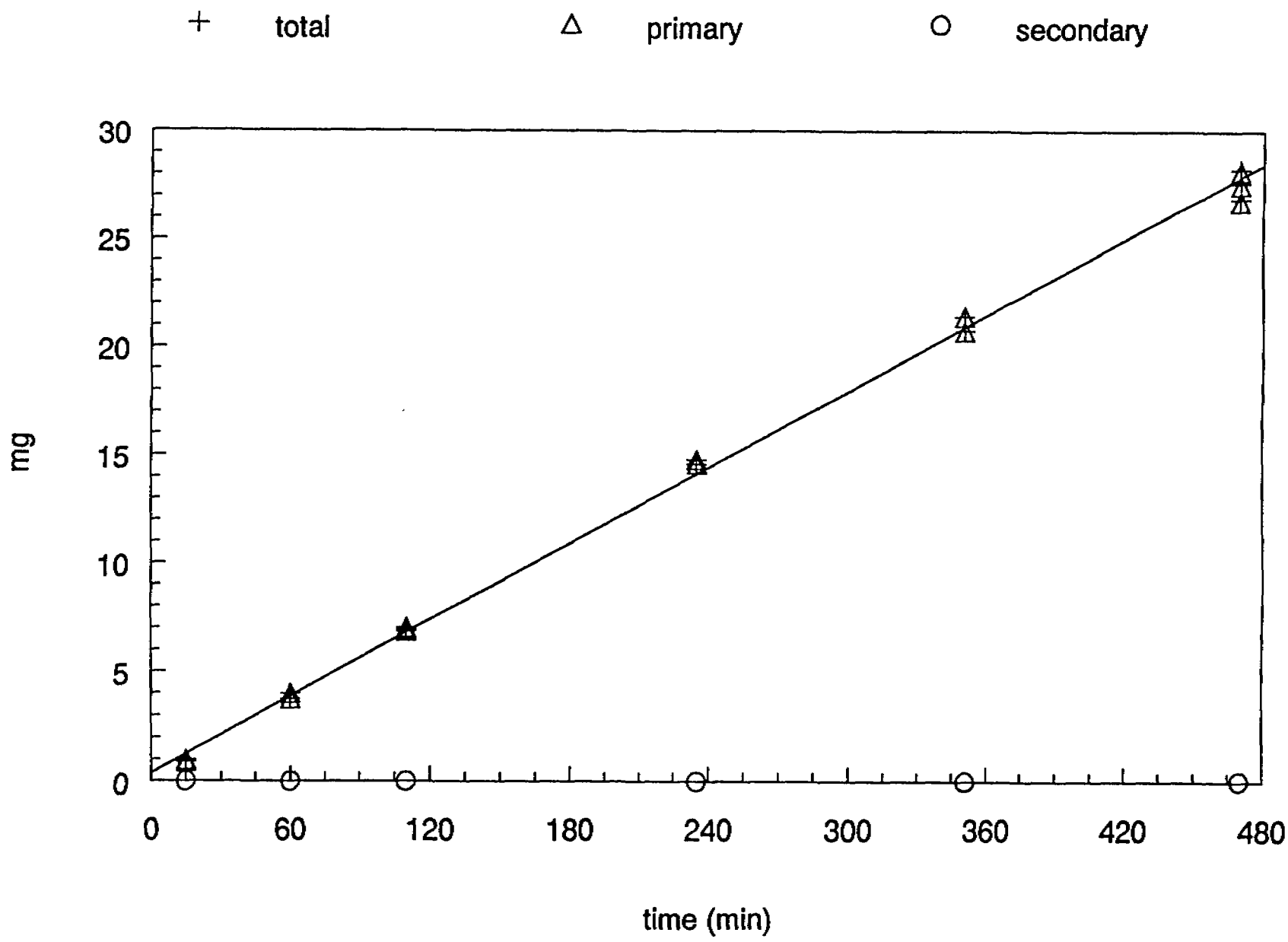
2.02731	2.174											
2.17388	2.331	2.172	0.140364									
1.92434	2.063											
1.98042	2.123											
1.95793	2.051	2.023	0.035564	1.996	0.095571	10						
1.89261	1.983											
1.94131	2.034											
1.79496	1.88	1.97	0.139715									
1.81283	1.899											
2.03437	2.131											
1.99337	2.088	1.922	0.153921	1.887	0.109311	60	small					
1.70338	1.784											
1.80727	1.893											
1.72088	1.803	1.851	0.048983									
1.81436	1.901											
1.76545	1.85											
2.76105	2.296	2.429	0.145965	2.429	0.145965	399	alum					
2.8937	2.407											
2.7101	2.254											
3.18293	2.647											
2.9372	2.443											
3.04077	2.529											
3.00425	2.132			2.227	0.10792	221	alum					
2.9362	2.084											
3.33468	2.367											
3.15633	2.24											
3.12722	2.219											
3.27171	2.322											
3.37871	2.148			2.124	0.110493	105	alum					
3.53563	2.248											
3.05727	1.944											
3.34085	2.124											
3.48948	2.219											
3.24541	2.064											
3.86996	2.289			2.169	0.135254	302	alum					
3.48862	2.063											
3.54756	2.098											

3.42883	2.028											
3.66405	2.167											
4.00981	2.371											
2.16591	2.072			2.148	0.121642	94	mod sm					
2.38476	2.281											
2.17588	2.081											
2.17778	2.083											
2.43134	2.326											
2.13983	2.047											
1.71664	2.118			2.063	0.148642	25	mod sm					
1.4895	1.838											
1.79993	2.22											
1.60569	1.981											
1.79323	2.212											
1.62921	2.01											
2.5669	1.822			2.032	0.173278	17	mod sm					
2.9666	2.105											
2.63741	1.872											
3.03423	2.153											
2.77427	1.969											
3.19705	2.269											
3.02999	1.938	1.779	0.162814	1.723	0.134696	3	fan died					
2.52125	1.612											
2.79362	1.787											
2.43123	1.555	1.667	0.097136									
2.70077	1.727											
2.68732	1.719											
3.26038	2.085	1.885	0.184616	1.854	0.17125	3						
2.69148	1.721											
2.89072	1.849											
3.0294	1.937	1.823	0.190681									
3.01627	1.929											
2.50654	1.603											
3.55451	2.08	2.202	0.129792	2.224	0.087839	340 w fan						
3.99627	2.338											
3.73995	2.188											
3.89665	2.28	2.246	0.031215									

3.82977	2.241											
3.79121	2.218											

1,1,1-Trichloroethane

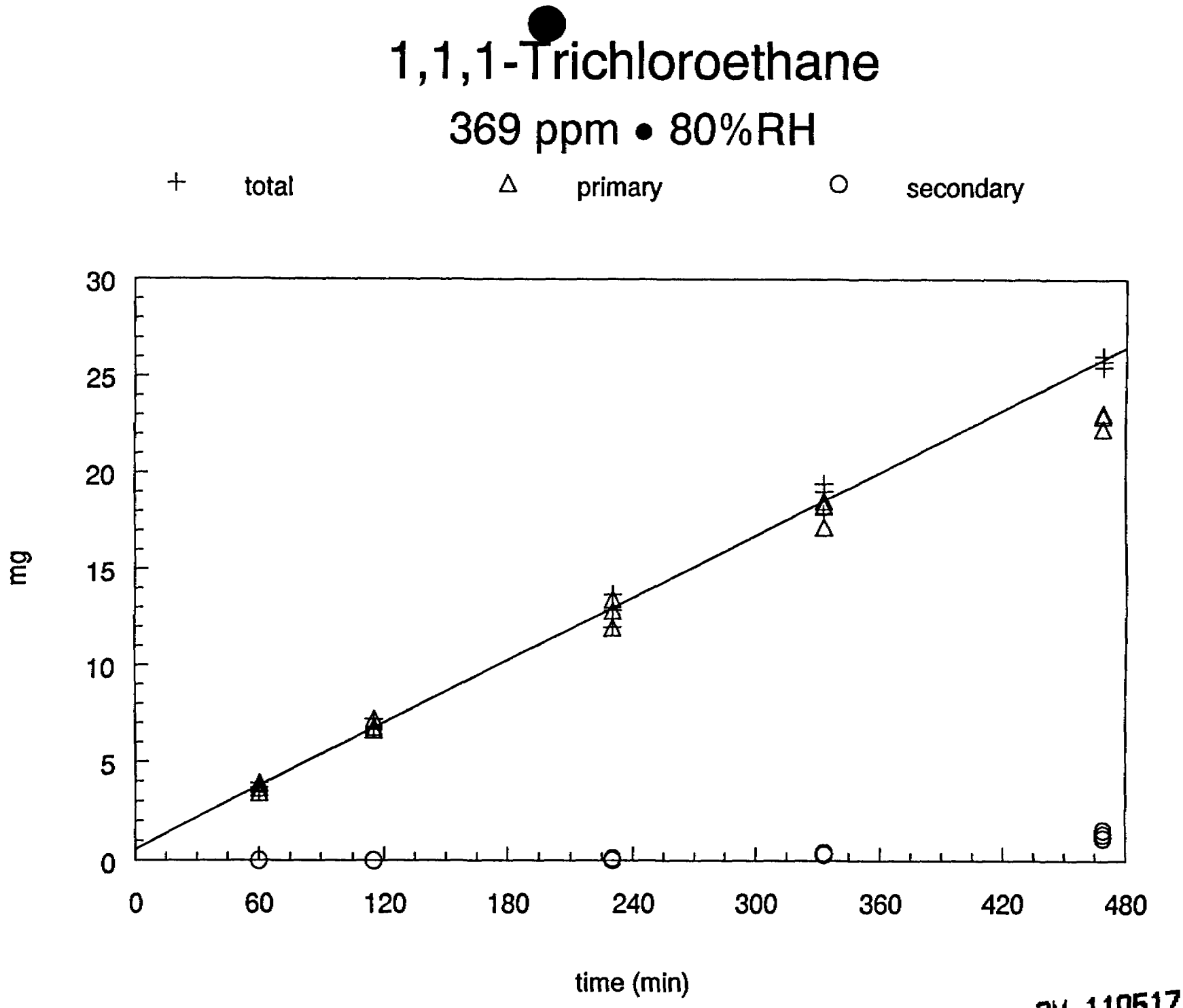
367 ppm • 50%RH



3M 110516

1,1,1-Trichloroethane

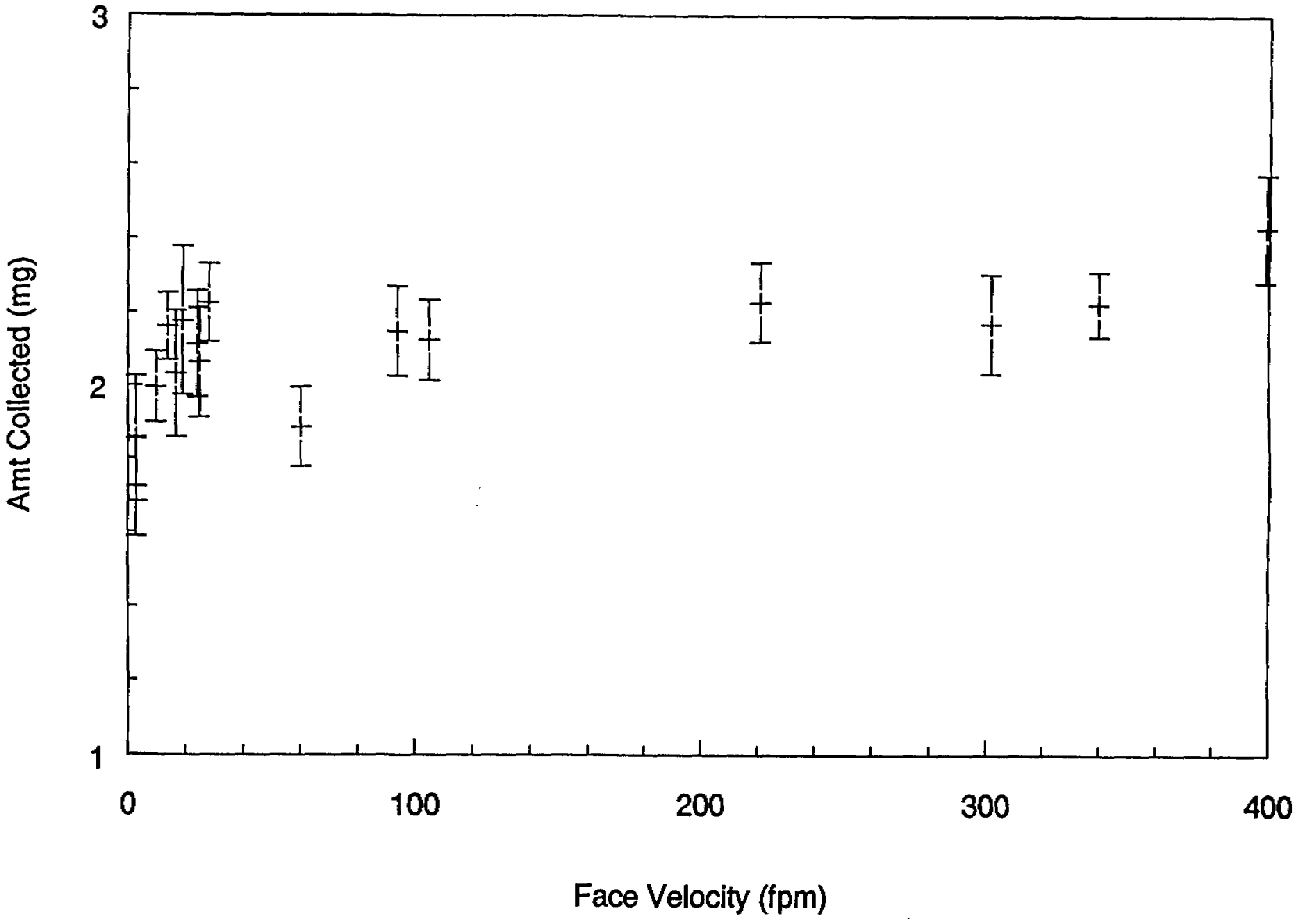
369 ppm • 80%RH



3M 110517

Face Velocity

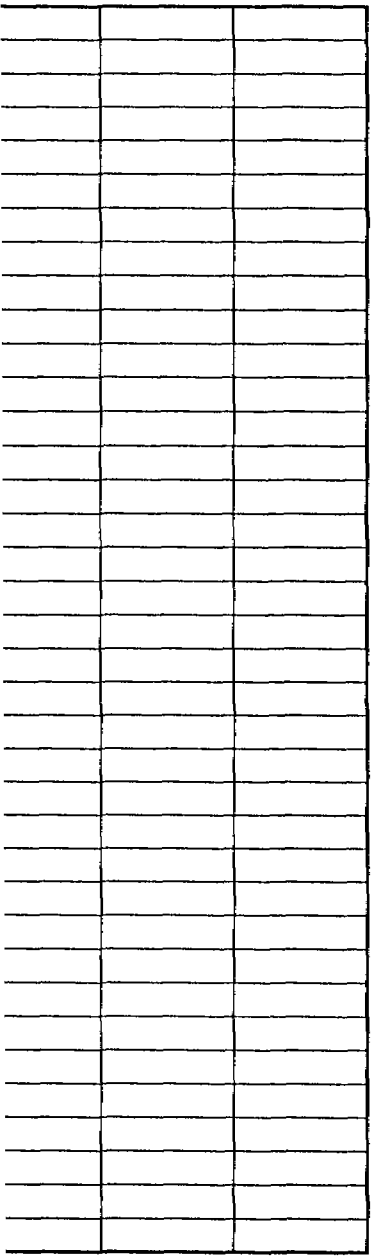
1,1,1-Trichloroethane 110 ppm 2 hrs



3M 110518

RECOVERY, STORAGE AND LONG TERM STORAGE NOVEMBER, 1995								ctcde3.xls	
EL	CCl4			CHCl3			1,2-DCE		
	SPIKE	UG	REC	SPIKE	UG	REC	SPIKE	UG	REC
0.1	47.7	62.3	1.30608	74.6	75.44	1.01126	62.8	65.58	1.044268
0.1	47.7	55.49	1.163312	74.6	73.04	0.979088	62.8	63.32	1.00828
0.1	47.7	60.06	1.259119	74.6	73.06	0.979357	62.8	64.71	1.030414
0.1	47.7	61.37	1.286583	74.6	77.37	1.037131	62.8	71.69	1.141561
0.5	238.5	262.72	1.101551	373	350.75	0.940349	314	305.38	0.972548
0.5	238.5	270.67	1.134885	373	358.68	0.961609	314	313.54	0.998535
0.5	238.5	264.53	1.10914	373	362.06	0.97067	314	311.71	0.992707
0.5	238.5	270.85	1.135639	373	364.64	0.977587	314	315.29	1.004108
1	477	528.75	1.108491	746	721.88	0.967668	628	621.91	0.990303
1	477	544.06	1.140587	746	730.25	0.978887	628	633.84	1.009299
1	477	526.63	1.104046	746	721.25	0.966823	628	619.57	0.986576
1	477	535.99	1.123669	746	732.84	0.982359	628	629.55	1.002468
2	954	1051.26	1.10195	1492	1433.58	0.960845	1256	1241.05	0.988097
2	954	1069.76	1.121342	1492	1439.27	0.964658	1256	1249.94	0.995175
2	954	1055.85	1.106761	1492	1431.91	0.959725	1256	1234.83	0.983145
2	954	1046.67	1.097138	1492	1420.15	0.951843	1256	1227.75	0.977508
AVE ALL			1.15			0.97			1.01
SD			0.07			0.02			0.04
CV			6.02			2.35			3.98

HUMIDITY EFFECT ON STORAGE @ .5EL							
Carbon Tetrachloride UG							
SPIKE	INIT DRY	INIT WET	2Wks RT	2Wks CO	3Wks RT	3Wks CO	
238.5	262.72	270.58	259.4	261.7	263.99	263.21	
238.5	270.67	267.93	265.29	266.12	258.78	262.01	
238.5	264.53	253.94	261.76	263.58	267.49	269.05	
238.5	270.85	258.39	259.78	268.34	263.47	268.67	
Carbon Tetrachloride Recovery							
	INIT DRY	INIT WET	2Wks RT	2Wks CO	3Wks RT	3Wks CO	
	1.10	1.13	1.09	1.10	1.11	1.10	
	1.13	1.12	1.11	1.12	1.09	1.10	
	1.11	1.06	1.10	1.11	1.12	1.13	
	1.14	1.08	1.09	1.13	1.10	1.13	
AVE	1.12	1.10	1.10	1.11	1.10	1.11	
SD	0.02	0.03	0.01	0.01	0.02	0.02	
Chloroform UG							
SPIKE	INIT DRY	INIT WET	2Wks RT	2Wks CO	3Wks RT	3Wks CO	
373	350.75	367.53	348.53	345.93	341.16	346.08	
373	358.68	357.14	354.65	347.02	338.22	344.35	
373	362.06	344.54	348.29	355.92	356.54	350.52	
373	364.64	349.44	351.65	353.68	348.26	356.19	
Chloroform Recovery							
	INIT DRY	INIT WET	2Wks RT	2Wks CO	3Wks RT	3Wks CO	
	0.94	0.99	0.93	0.93	0.91	0.93	
	0.96	0.96	0.95	0.93	0.91	0.92	
	0.97	0.92	0.93	0.95	0.96	0.94	
	0.98	0.94	0.94	0.95	0.93	0.95	
AVE	0.96	0.95	0.94	0.94	0.93	0.94	
SD	0.02	0.03	0.01	0.01	0.02	0.01	



3M 110520

1,2-Dichloroethane UG						
SPIKE	INIT DRY	INIT WET	2Wks RT	2Wks CO	3Wks RT	3Wks CO
314	305.38	316.79	314.72	315.68	312.08	316.13
314	313.54	312.15	322.99	313.17	308.13	313.23
314	311.71	299.56	316.72	319.88	325.35	321.28
314	315.29	304.18	319.11	319.43	317.97	326.98
1,2-Dichloroethane Recovery						
	INIT DRY	INIT WET	2Wks RT	2Wks CO	3Wks RT	3Wks CO
	0.97	1.01	1.00	1.01	0.99	1.01
	1.00	0.99	1.03	1.00	0.98	1.00
	0.99	0.95	1.01	1.02	1.04	1.02
	1.00	0.97	1.02	1.02	1.01	1.04
AVE	0.99	0.98	1.01	1.01	1.01	1.02
SD	0.01	0.02	0.01	0.01	0.02	0.02

3M 110521

LONG TERM STORAGE @ 1EL							
Carbon Tetrachloride							
	Initial						
Spike	ug	rec					
477	523.61	1.097715					
477	515.59	1.080901					
477	523.04	1.09652					
477	525.46	1.101593					
477	511.93	1.073229					
477	520.19	1.090545					
ave	519.97	1.09					
sd	5.228556	0.01					
Chloroform							
	Initial						
Spike	ug	rec					
746	713.72	0.956729					
746	695.79	0.932694					
746	714.46	0.957721					
746	721.01	0.966501					
746	701.05	0.939745					
746	712.29	0.954812					
ave	709.72	0.95					
sd	9.399472	0.01					

3M 110522

1,2-Dichloroethane									
	Initial								
Spike	ug	rec							
628	619.13	0.985876							
628	606.81	0.966258							
628	621.57	0.989761							
628	625.84	0.996561							
628	611.53	0.973774							
628	615.93	0.98078							
ave	616.8017	0.98							
sd	6.902656	0.01							

Fax Cover Sheet

To:Christine Dalton

Company:Industrial Hygiene Lab

Fax:011 49 6371 868 788

From: Donald J. Larsen

Phone: 612-737-4103

3M Occupational Health and Environmental Safety Division
3M Center Bldg. 260-3B-08
St. Paul, MN 55144

Fax: (612)737-3069

Number of pages including cover sheet: _1_____

Message: On September 28 we discussed your concerns about low recoveries for halogenated anesthetics. I ran some recoveries for Halothane, Ethrane and Forane at levels from 73 to 281 ug spiked on the monitors and found recoveries from 84 to 115 % as shown in the following table:

Compound	Spike (ug)	Recovery
Halothane	94	1.15
	187	1.01
	281	1.05
Ethrane	76	0.93
	152	0.84
	228	0.86
Forane	73	0.93
	145	0.84
	217	0.86

Please contact me if you continue to experience low recoveries.
Best regards, Don Larsen, CIH

EVALUATION OF DIFFUSIVE SAMPLERS FOR MONITORING TOXIC GASES AND VAPOURS IN COALMINES

Institute of Occupational Medicine Ltd, Edinburgh

3M - INTERNAL CORRESPONDENCE

dc: R. Pieper

To: J. Palazzotto
From: D. Larsen
Subj: OVM Validation by Institute of Occupational Medicine, Ltd., Edinburgh

Date: March 26, 1991

I reviewed the following report which compares the 3M 3500, Perkin-Elmer ATD 50, SKC 530, Draeger ORSA 5, MSA OVD, and PRO-TEK G-BB diffusion monitors.

INSTITUTE OF OCCUPATIONAL MEDICINE LIMITED
8 Roxburgh Place
Edinburgh
EH8 9SU

EVALUATION OF DIFFUSIVE SAMPLERS FOR MONITORING TOXIC GASES AND VAPOURS IN COALMINES

by D. Mark, A. Robertson, H. Gibson, G. Borzucki, B. Cherrie, and W. M. Maclaren

September, 1990

Diffusion monitors were evaluated for effects due to windspeed, orientation, vapor loading, fluctuating concentration, and airborne dust. Only the 3M 3500 gave acceptable results for all the tests. Windspeeds from 1-12 m/sec (197-2362 fpm) at orientations of 0^{o} and 90^{o} did not affect the 3M 3500 sampling rate. The 3M 3500 also exhibited low bias, low variability, and was unaffected by turbulence or airborne dust. The monitor did not show any significant loss when an initial 240 ppm 1,1,1-trichloroethane spike for 10 minutes was followed by 470 minutes at 0 ppm.

The Pro-Tek G-BB showed high variability and was very dependent on windspeed. The authors suggested that the diffusion barrier was not adequate to prevent these effects. The monitor worked so poorly in the initial tests that it was not tested further.

The MSA OVD also showed high variability and bias in the windspeed and orientation tests.

The Draeger ORSA 5 was effected significantly by high windspeeds and turbulence.

The Perkin-Elmer ATD 50 and SKC 530 sampling rates supplied by the manufacturer did not agree with the experimental rates. The PE ATD 50 showed a large consistent low bias and the SKC 530 a large high bias. The SKC 530 also showed some orientation effects on sampling rate and variability.

This report concludes that the 3M 3500 was the only diffusion monitor which performed acceptably in all their tests.

Report No. TM/90/11
UDC 543.27:622.411.3

EVALUATION OF DIFFUSIVE SAMPLERS FOR MONITORING TOXIC GASES AND VAPOURS IN COALMINES

by

D Mark
A Robertson
H Gibson
G Borzucki
B Cherrie
WM Maclaren

September 1990

Price: £40 (UK)
£45 (Overseas)

Report No. TM/90/11
CEC CONTRACT 7260/04/028/08

INSTITUTE OF OCCUPATIONAL MEDICINE LIMITED

EVALUATION OF DIFFUSIVE SAMPLERS FOR MONITORING TOXIC GASES AND VAPOURS IN COALMINES

by

D Mark, A Robertson, H Gibson, G Borzucki,
B Cherrie, WM Maclaren

FINAL REPORT ON CEC RESEARCH CONTRACT 7260/04/028/08

Duration of project: March 1986 to February 1989

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September 1990

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INSTITUTE OF OCCUPATIONAL MEDICINE

Final Report on CEC Research Contract 7260/04/028/08

EVALUATION OF DIFFUSIVE SAMPLERS FOR MONITORING TOXIC GASES AND VAPOURS IN COALMINES

by

D Mark, A Robertson, H Gibson, G Borzucki,
B Cherrie, WM Maclaren

SUMMARY

Diesel engines, resins and cleaning agents, which can all give off hazardous gases and vapours, are being used increasingly in British coalmines. With the increasing awareness of the potential risks to health associated with these materials it may, therefore, be necessary to monitor a wide range of gases and vapours in coalmines in the future, There are many procedures capable of sampling and analysing toxic gases and vapours in coalmines. Diffusive (or passive) samplers are particularly attractive because of their size and simplicity (no electrical pump is needed), ease of use and low cost. However, validation studies of these devices have not covered the relatively harsh environmental conditions encountered in coalmines and there is a dearth of information on their performances at high windspeeds, in turbulent air and in dusty atmospheres.

The aim of this study was to investigate whether diffusive sampling offered a practical solution to sampling toxic gases and vapours in coalmines by studying the performances of a range of diffusive samplers under such conditions.

A series of laboratory tests were, therefore, carried out in wind tunnels to determine the effects of windspeed, sampler orientation, turbulence, fluctuating vapour concentrations and dust on the performances of six commercially available diffusive samplers (SKC 530, 3M 3500, Drager ORSA 5, Dupont Protec G-BB, MSA OVD and Perkin Elmer ATD50). A limited underground field exercise was also undertaken to validate the laboratory work.

The results of the research have clearly demonstrated that diffusive sampling could be used successfully to monitor toxic gases and vapours in the harsh environmental conditions which prevail in coalmines and that diffusive samplers are potentially flexible, simple and cheap tools for this purpose.

There are difficulties. In tests with only two vapours, just one sampler of the six tested (the 3M 3500) performed to its specification. (This device, we believe, is the most suitable for coalmine use). One did not perform as a static sampler in harsh conditions, two required recalibration and two were unsatisfactory. It is therefore essential that, before a diffusive sampler is used to measure any gas or vapour, independent validation data are obtained.

1. BACKGROUND

1.1 Introduction

The sampling of gases in coalmines usually concerns methane and carbon monoxide, and well-proven methods are employed for this purpose. However, with the increasing use underground of diesel engines, resins, and cleaning agents which may produce hazardous gases or vapours, and the increasing awareness of their potential risks to health it may be necessary in the future to carry out regular monitoring of a wide range of gases and vapours.

There are many techniques available for monitoring gases and vapours. Direct reading methods, which range from the simple colorimetric detector tubes to the complex electrical instruments can be used, but there are difficulties. Detector tubes, whilst cheap and easy to use, are subject to interferences from other gases, and have low precision. Electrical instruments can be selective, accurate, and precise, but are expensive to purchase particularly when large numbers of sampling sites are required. Stringent intrinsic safety requirements for the use of electrical instrumentation underground in coalmines is also a problem. Alternative methods of measuring gases and vapours in coalmines usually involve their collection in an absorptive medium which is returned to the central laboratory for analysis. For toxic organic vapours and gases sampling is commonly carried out by drawing a known volume of air through a small tube containing an adsorbent material (frequently charcoal) using a small battery-powered pump. Analysis is mainly by gas chromatography after chemical desorption. This procedure is commonly known as the NIOSH tube method (NIOSH, 1984). The method is precise, accurate and relatively inexpensive, but it does require the purchase and maintenance of intrinsically-safe pumps, and in practice only 10 - 20 samplers can be supervised by one investigator.

Diffusive samplers (sometimes called passive samplers) appear to be an attractive alternative provided that their validity and reliability under mine conditions can be established. Diffusive samplers, like conventional pumped samplers, work on the principle that the gas to be monitored is absorbed in or adsorbed on a medium for laboratory analysis. Where they differ is the way in which the toxic gas arrives at the adsorbent surface. In diffusive samplers the airborne molecules of gas are transported to the surface in question by the action of molecular diffusion in the concentration gradient which exists in the surface and the atmosphere being sampled. There is therefore no need for a sampling pump, and consequently diffusive samplers are simpler and easier to carry and deploy in the workplace. However, they are more expensive to buy than the standard NIOSH tubes used with the pumps. Diffusive samplers are finding increasing applications in surface industries (e.g., oil, chemical, etc.,), and the performances of a number of different devices have been reported widely. Validation protocols have been proposed both in Britain (HSE, 1987) and in the USA (Cassinelli *et al*, 1987) to establish their performances. The test conditions specified in these protocols concentrate on their performance in little air movement because, when exposed to conditions of low windspeeds (<0.2 m/s), undersampling occurs due to the

depletion of the vapour concentration in front of the sampler. No account is taken of the more severe conditions found in coalmines. In particular there is a dearth of experimental information about how diffusive samplers perform in airflows where the velocities are high, the orientations are variable, the turbulence levels are high, and there are considerable quantities of airborne dust.

The purpose of this project was to investigate the performances of a range of diffusive samplers under such conditions. Experiments were carried out mainly in the laboratory where a range of mine environmental conditions were simulated in wind tunnels and exposure chambers. A field trial with the most promising diffusive samplers was conducted in one colliery location.

1.2 Theoretical Considerations

Although, as will be seen below, this project is not intended as a basic study of the physical processes governing the performances of diffusive samplers, a short review of the principles of operation of the various types of device will be a useful basis for interpreting the results of the experimental enquiry. Here therefore, a short review of the theoretical background is given.

1.2.1 Basic concepts

Diffusive samplers operate on the principle that, if a concentration gradient exists for a molecular species (e.g., a gaseous contaminant), then there will be a net flux of that species from regions of high to regions of low concentration. This well-known phenomenom is described in classical kinetic theory by Fick's law, by which the flux is proportional to the concentration gradient and the constant of proportionality is known as the molecular diffusion coefficient. The latter is a fundamental property of the contaminant in question, also derivable from classical kinetic theory.

There are two basic categories of diffusive sampler. The tube-type device first proposed by Palmes and Gunnison (1973) is shown schematically in Figure 1.1. Here the gradient which drives the molecular flux is set up along the length of a tube, one end of which is exposed to the contaminant of interest and the other end of which is maintained at a lower concentration due to the presence of an adsorbent surface. From Fick's law, the mass transfer rate to the sorbent (M) is

$$M = D A (dc/dx) \qquad (1)$$

where D is the molecular diffusion coefficient for the contaminant, A the cross-sectional area of the diffusion path, and dc/dx the gradient of the concentration (c) along the diffusion path (x-direction). For a diffusion path L and a perfect sorbent (so that $c \rightarrow 0$ at its surface), then this becomes

$$M = D A (c/L) \qquad (2)$$

For a sampler which has been exposed for a time t, then the time-averaged concentration of the contaminant in the air outside the sampler may be obtained from measurement of the mass collected. That is

$$\bar{c} = m L / D A t \qquad (3)$$

where m is the mass of contaminant collected and we require to know the value of D. For tube-type diffusive samplers, theoretical values of D (based on kinetic theory) can provide accurate measurements of concentration.

In the permeation-type devices proposed by Nelms *et al* (1977) and Bailey *et al* (1977), the concentration gradient is established by the placement of a membrane immediately in front of the sorbent (as shown in Figure 1.2). Once again, transfer follows Fick's law, this time leading to

$$\bar{c} = K m / t \qquad (4)$$

where K is the permeability coefficient for the membrane used, embodying both its dimensions (thickness and cross-sectional area) and the coefficient of molecular diffusion for the transfer of the contaminant across it. For practical diffusive samplers operating under this principle, K is usually determined experimentally for each sampler and for each contaminant.

1.2.2 Modifying influences to the simple theory

Sorbent efficiency:

The assumption of a perfect sorbent may not hold in practice. For example, it has been found that, for devices where organic vapours are adsorbed onto a carbon collecting medium, the sampling rate is dependent on the amount of gas already adsorbed. The concept of an adsorption isotherm has been introduced to describe this problem. The simplest is the linear isotherm, where the vapour pressure at the surface of the sorbent is directly proportional to the mass of sampled

contaminant. Underhill (1984) has shown that, under these conditions, the rate of uptake by a tube-type device like that described earlier takes the form

$$dm/dt = (D\ A\ C\ /\ L)\ \{1 - (m\ /\ k\ C)\} \qquad (5)$$

where k is a constant coefficient dependent on sampler properties. Equation (5) shows clearly the fall in sampling rate as the contaminant builds up in the sorbent.

Time-varying concentrations:

The simple theory also assumes that the concentration of the contaminant outside the sampler is fixed. In practice, however, it would usually vary with time. The problem of varying concentrations was first addressed by Hearl and Manning (1980), whose main concern was the transient response of the sampler (where the contaminant concentration is fixed, but for a finite time which may be long or short). They showed that, although Equation (1) holds well for long sampling periods, the contaminant is progressively undersampled for shorter sampling times. In addition to being a function of sampling time, the error is also a function of sampler geometry and dimensions. Typically, for a tube-type sampler of length 7 cm, the undersampling error involved in the collection of NO_2 is less than 1% for a sampling time of five hours, but rises to greater than 10% for a sampling time of 15 minutes.

A similar problem occurs when the nature of the concentration variation takes the form of random fluctuations. Here, the sampling error is a function of the statistical properties of the fluctuating concentration. Bartley *et al* (1983) have examined theoretically the fluctuation-induced sampling error for a tube-type sampler containing a perfect sorbent. They referred to the 'pulsating' nature of fluctuating concentrations, and showed that the error increases with the degree of 'sharpness' of the pulses, although the error may be reduced if sampling takes place over longer periods. For shorter sampling periods, however, the error may be reduced by shortening the tube length (L). The nature of the errors deserves comment. In general, there is a tendency towards undersampling, corresponding to contaminant diffusing out of the sampler during intervals when the concentration gradient is unfavourable for collection. However, oversampling can occur when large pulses arrive near the end of the sampling period.

Bartley (1983) examined the problem of weak sorbents together with fluctuating concentrations and showed that errors can arise due to a combination of the effects summarised above. His analysis showed that such errors can be significantly reduced by appropriate modifications to the sampler design, in particular the use of multiple sorbent stages. Such a system provides the added benefit that any saturation of the sorbent can be detected and - where necessary - the results obtained may be discarded.

Effects of an external wind:

In the absence of any external air movement, the contaminant concentration is underestimated by a diffusive sampler as the source molecules in the immediate vicinity of the device are depleted by the flux to the sorbent. A finite air movement outside the sampler is therefore essential in order to replenish the 'pool' of contaminant on which the sampler depends for its operation. It has been estimated that a windspeed of a few cm/s would suffice for this purpose, needing to be higher for samplers of higher uptake rate. The effects of moving air at higher velocities are not well understood; neither are the effects of turbulent fluctuations in the wind velocity. It is recognised that any external wind effects sufficient in magnitude to induce air motions within the diffusion gap (e.g., the tube of a tube-type device) may well interfere with 'normal' sampler performance. However, it has been suggested that, for tube-type samplers, any such effects would be minimised by ensuring that the length-to-diameter ratio is less than about 3 (Coleman, 1983). Otherwise, the use of a wind shield might have the same desired effect.

Effects of relative humidity:

It has been suggested that humidity might effect the collecting properties, notably the adsorption capacity, of some sorbents (e.g., activated carbon, as reported by Werner, 1985). The mechanism is thought to involve competition between adsorption sites between contaminant and water molecules, but at present it is not well understood.

Effects of other contaminants:

The influence of competing gaseous species has already been alluded to (i.e., contaminant versus water molecules). A similar effect would occur if more than one gaseous contaminant is present (e.g., competing solvent vapours, as discussed by Gregory and Elia, 1983). In the underground mining application of diffusive samplers which is the subject of this report, a prominent airborne contaminant which might well influence sampler performance is airborne dust. At present, however, any effects of the presence of dust particles (e.g., on the surface of the sorbent) are not known.

2. AIMS OF PROJECT AND PROJECT PLAN

The main aim of the project was to determine whether and under what conditions any of the currently, commercially–available (in Britain) diffusive samplers are suitable for monitoring toxic gases and vapours in coalmines. The following project plan was adopted:–

1. Select suitable types of commercially–available diffusive sampler.

2. Select suitable test vapours.

3. Identify environmental conditions specific to coalmines that are likely to effect the performance of diffusive samplers.

4. Construct and commission exposure chambers.

5. Investigate the effect of high windspeeds and variable orientation on the performances of the diffusive samplers.

6. Decide, on the basis of these tests, whether any of the devices are entirely unsuitable for use underground and should be omitted from further testing.

7. For the successful samplers investigate the effect on their performances of variable vapour loading, turbulent airflows, fluctuating vapour concentrations, airborne dust exposure.

8. Investigate the performances of the most suitable types of diffusive sampler in limited underground trials at selected colliery locations.

9. From the results of the above investigations make recommendations as to whether and under what conditions diffusive samplers may be used underground to monitor toxic gases and vapours.

3. THE DIFFUSIVE SAMPLERS

Six commercially available diffusive samplers of different design were tested. The choice was influenced firstly by the requirement to evaluate the performance of currently available samplers, and secondly in order to form a rational basis for choosing diffusive samplers from future designs. Brief descriptions of the important features of each sampler are presented below.

3.1 SKC 530: Manufactured by SKC Inc.(USA) – Figure 3.1

This device consists of a reusable plastic badge housing holding two adsorbent capsules behind two circular sampling windows of cross-sectional areas in the ratio 13:1. This enables two simultaneous samples to be taken at two different sampling rates (in proportion to the cross-sectional areas), and therefore it is possible to cover both high and low vapour concentrations with one device. The sampling windows are covered with porous plastic material to minimise external wind effects. The adsorbent capsules contain a fixed weight of activated charcoal sandwiched between discs of urethane and stainless steel gauze.

3.2 3M 3500 OVM: Manufactured by 3M Company (USA) – Figure 3.2

This unit consists of a round nylon body, approximately 45 mm diamter, containing a circular adsorbent pad based on charcoal, separated by spacers from a diffusion membrane – the distance between the membrane and adsorbent being the diffusion length. Contaminants reach the adsorbent by first permeating through the membrane wind shield before diffusing across the air gap. Another version of this design (3520 OVM), which has a second back-up adsorbent pad in series with the first, is available for demanding environments.

3.3 MSA OVD: Manufactured by Mine Safety Applicances Company (USA – Figure 3.3)

This badge consists of a rectangular plastic case 12 mm by 72 mm in which are housed two activated carbon sampling strips and a separator. The case is sealed with a plastic top, which is perforated with five large rectangular holes behind which sits a paper windshield. Like the 3M device the first sampling strip is separated from the windshield with spacers, thus providing a diffusion path length. The second sampling strip provides a back-up for when the first strip becomes saturated.

3.4 Drager ORSA 5: Manufactured by Drager (West Germany) - Figure 3.4

The sampling section of this device consists of a glass tube 7.5 mm in diameter and 28 mm long, containing a fixed quantity of grains of activated charcoal held centrally within the tube by porous plugs at each end. The plugs form the diffusion path lengths over which the gas/vapour diffuses, from both ends simultaneously, to the adsorbent. The device can be used as a pumped tube sampler when higher sampling rates are required. When used in its diffusion mode the sampling section is mounted in a plastic holder which incorporates an attachment clip.

3.5 Dupont PROTEC G-BB: Manufactured by Dupont (USA) - Figure 3.5

This device comprises two identical, rectangular sections (12 mm by 75 mm) in series. Each section consists of an uptake control block (a plastic strip perforated with 281 holes: 1.1 mm diameter) held in intimate contact with an adsorbent strip based on activated charcoal. Vapour molecules diffuse along the tubes formed in the control block to give an uptake rate proportional to the ambient vapour concentration and a function of the length and cross-sectional area of the holes. The second section is utilised only when the first becomes overloaded and the vapour molecules pass through the first section to repeat the process of diffusion and adsorption in the second strip. The uptake rate of the second strip is less than that of the first because of the extra distance the molecules must diffuse. In situations where vapour concentrations are low and/or short sampling times are involved the second adsorbent strip, together with the rear sealing cover, can be removed to form a 'sandwich' from the control blocks and the single adsorbent strip; vapour can now reach the adsorbent strip from two routes and the uptake rate is doubled.

3.6 Perkin Elmer ATD50: Manufactured by Perkin Elmer Ltd (UK) - Figure 3.6

This device is a direct development of the original Palmes tube, consisting of a precision-made, stainless steel tube, 90 mm long and 5 mm internal diameter containing a carefully-weighed amount of Tenax GC (or similar) adsorbent material. At one end of the tube an aluminium sampling head is fitted, incorporating a semi-permeable silicon membrane and a stainless steel gauze. The distance between the surface of the adsorbent and the membrane defines the diffusion path length, which is carefully-controlled to be 15 mm. The combination of membrane and stainless steel gauze within the sampling head is designed to minimise external wind effects, and to inhibit the ingress of water vapour and particulate matter. These samplers have been developed specifically for analysis incorporating thermal desorption.

4. EXPERIMENTAL EQUIPMENT AND METHODS FOR LABORATORY EXPERIMENTS

4.1 Exposure

4.1.1 Exposure chamber

One exposure chamber was used for the investigations. This comprised a wooden wind tunnel, shown schematically in Figure 4.1, 2.7 metres long and 0.35 metres square cross-section, which was used to examine the wind-dependent characteristics of the diffusive samplers. Air was drawn through the tunnel by a continuously variable-speed axial fan which produced airspeeds within the range 1 to 12 m/s. Velocity was measured using a hot-bead anemometer which had been previously calibrated using a pitot-static tube and micromanometer. Removable honeycomb sections 50 mm thick and 6 mm mesh size, positioned either side of the exposure area, were used to reduce the turbulent kinetic energy in the exposure area to a level such that turbulent intensities in the x-direction were around 3%.

The vapour generator system (see Figure 4.2) was positioned at the tunnel intake and produced test vapour by evaporating droplets of the liquid in an air stream. Th system consisted of an evaporating/mixing manifold, a spinning disc rotated by an air-turbine, an air blower, and five vapour-dispersive pipes.

Droplets with a nominal diameter of 25 μm were produced by injecting the liquid onto the centre of the rotating disc from where it spread to the perimeter and disintegrated under the centrifugal force produced by the rotation. A constant liquid flowrate to the disc was maintained by either a constant head gravity feed arrangement or syringe pump. Air blown continuously into the manifold facilitated droplet evaporation and produced vigorous mixing before transporting the vapour out through the five dispersive pipes. Each pipe consisted of a 15 mm diameter copper tube, bent to form the shape shown in Figure 4.2, and perforated with a total of 24 4 mm diameter holes equidistantly spaced along the top and underside of the tube. The five pipes were positioned directly in front of the tunnel entrance so that the straight sections ran horizontally across the width of the tunnel entrance and were equally spaced in the vertical plane as can be seen in Figure 4.2.

During operation this arrangement of pipes and emission holes produced a continuous vapour 'sheet' across the entrance which was drawn into the tunnel and distributed across the tunnel cross-sectional area (in the mixing length) before passing into the exposure area. A vapour concentration distribution, uniform to ± 10%, was invariably achieved across the wind tunnel using this vapour generation method.

For the laboratory studies 1,1,1 trichloroethane (methyl chloroform) was used to generate test vapour clouds in the wind tunnel in concentrations ranging from 5 to 240 ppm. This solvent was chosen after a study of the chemicals used

underground in coalmines showed it to be the most widely used. It also has the benefit of being relatively non-toxic, and easy to handle.

In the exposure area the diffusive samplers to be tested were mounted at six locations on a stainless steel frame as shown in Figure 4.3. At each location a NIOSH-type pumped-tube sampler and an inlet pipe to a flame ionisation detector (FID) were fixed close to the diffusive sampler under test.

For some investigations isotropic turbulence in the air approaching the exposure area was generated by means of inserting square-mesh grids in the wind tunnel between the entry and the exposure area. By careful choice of bar width and distance between the grids and the samplers a range of turbulence conditions was obtained. For these runs the honeycomb sections were removed.

For another set of investigations airborne dust clouds were produced by injecting test powders into the entry of the wind tunnel (see Figure 4.1) by means of either a Wright dust feeder (Wright, 1954), or a turntable-venturi dust feeder, dependent upon the type of dust.

4.1.2 Reference samplers

The main device chosen to give a measurement of the true vapour concentration and thus to serve as the reference sampler for the investigations was the SKC Sorbent Tube. This device, shown in Figure 4.4 and built in accordance with the NIOSH/OSHA-approved method for sampling vapours in the workplace (NIOSH, 1984), comprises a thin glass tube (6 mm diameter and 70 mm long) which contains a precisely-controlled quantity (150 mg) of coconut-base charcoal sorbent material separated into two sections: one for sample collection (100 mg); and the other for back-up to assure complete vapour collection (50 mg). For some experiments, especially those using high vapour concentrations and/or long sampling times larger identically-constructed tubes (8 mm diameter and 110 mm long) were used. These tubes each contained 400 and 200 μg of charcoal in the front and rear sections respectively.

Suction through the samplers, at a flowrate of approximately 80 ml/min was provided by a main vacuum pump via a multi-outlet manifold. Flowrate control was achieved by suitable restrictive orifices inserted into each sampling line. Flowrate measurement was carried out before and after exposure using a primary standard automatic bubble flowmeter (Dupont Buck Calibrator).

Vapour concentrations were also monitored using a Flame Ionisation hydrocarbon analyser (Analysis Automation Ltd., Model 521). This was used to establish the initial levels of vapour concentration and to monitor those levels throughout the duration of exposure. Concentration levels from up to seven locations were monitored sequentially on a cycle controlled by a BBC microcomputer, which also logged the individual values and displayed the running means and standard deviations for each particular sampling location. Any departures from the required target concentration were thus quickly detected and rectified.

4.1.3 General procedures

To ensure the quality control of the experiments two examples from each new batch of samplers were chosen and set aside to check for contamination. During this procedure two batches of Drager ORSA 5 samplers were found to be contaminated with the test solvent on delivery.

At the end of the exposure period the test vapour was switched off first, the various samplers capped as quickly as possible, and stored in a refrigerator.

A comprehensive labelling and recording procedure was developed to ensure that the samplers were not mis-identified.

4.2 Analytical Procedures

The analytical procedures involved firstly the desorption of the captured solvent from the adsorbent material, and secondly the analysis of that solvent by gas chromatography.

For analysis of the NIOSH pumped tubes and the diffusive samplers, apart from the Perkin Elmer ATD50, solvent desorption processes were employed. Slightly different procedures were adopted dependent upon the type of sampler involved. With the MSA OVD, the Dupont Protec, the Drager ORSA 5, and the SKC 530 diffusive samplers the charcoal adsortive strips were removed from their holders and placed in a 5 ml glass septum vial. 2 ml of carbon disulphide (Rathburn glass distilled, benzene-free), containing chloroform as an internal standard, were added to the charcoal using a precision gas-tight syringe. Samples were shaken for 30 minutes in a desorption shaker prior to analysis on the gas chromatograph. A similar procedure was adopted with the 3M 3500 diffusive sampler, except that desorption was carried out in the sampler body following removal of the permeable membrane. After desorption was complete (normally 30 minutes) the solution was transferred to a 5 ml septum vial ready for analysis.

All analyses were carried out by gas chromatography using an Analytical-Instruments Model 93 gas chromatograph. It was operated under the following conditions:-

Injector temperature	200 C
Column	2m x 4 mm glass tube packed with 12% carbowax 1540 on 80/100 mesh Chromosorb W
Carrier gas	Nitrogen
Oven temperature	55 C
Detector	Flame ionisation held at 200 C.

Adsorption peaks were recorded on a y-t chart recorder. Calibration standards were prepared by adding measured volumes of the test solvent Analar grade 1,1,1

trichloroethane, using a SGE microlitre plunger-in-needle syringe, to 2 ml of the carbon disulphide with chloroform as internal standard. Three calibration solutions were prepared for each run and the ratios of the peak heights from the 1,1,1 trichloroethane and the chloroform were measured and plotted against the known masses of 1,1,1 trichloroethane injected. Normally, linear relationships were found that went through the origin and the slopes of these lines represented the calibration constants to be used for each specific sampler.

The Perkin Elmer ATD50 samplers were thermally desorbed using a Spantech GN Concentrator Mark IV in a stream of nitrogen at 250 C for five minutes and the sampled solvent was collected in a cold trap containing Tenax adsorbent material which was held at -30 C. The cold trap was then flash-heated to 250 C and flushed with nitrogen for 20 seconds, to pass the desorbed solvent into the gas chromatograph via a pipe heated to 190 C. Once in the gas chromatograph analytical conditions and procedures were the same as those described above, apart from the calibration. The calibration procedure in this case involved the volatilisation of known quantities of trichloroethane injected into an airstream of known flowrate. A measured portion of the resultant mixture was drawn at 20 ml/min through the Perkin Elmer samplers thereby giving a known mass of the trichloroethane in the device. The standards were analysed by thermal desorption and gas chromatography and the calibration constant calculated. Again three calibration points were evaluated for each different experimental condition.

Desorption efficiencies for the various types of diffusive sampler were determined by injecting known quantities (0.5 ml) of 1,1,1 trichloroethane into a glass septum vial, containing the adsorbent material, using the microlitre syringe. Analysis of the adsorbed vapour was then determined by the above methods and the resultant masses of vapour compared to those injected. Desorption efficiencies very close to unity were obtained for all types of sampler, with values of 1.00 ± 0.02.

The masses (M) of 1,1,1 trichloroethane in the actual samples were calculated from the following equation:-

$$M = P\ G\ p\ /\ E \qquad (6)$$

where P is the ratio of peak heights 1,1,1 trichloroethane/chloroform, G is the calibration constant, p is the density of 1,1,1 trichloroethane, and E is the desorption efficiency. Calculation of the concentration was achieved from knowledge of the volume of air sampled. This was obtained by multiplying the uptake rate (Q), quoted by the manufacturers of the diffusive sampler, by the sampling period (t).

$$C = P\ G\ p\ /\ E\ Q\ t \qquad (7)$$

To ensure quality control of the analytical procedures, blanks and calibration samples were run daily. Initially all analyses were carried out in duplicate, but after the usual 'teething problems' were resolved, agreement between the two samples was invariably within 3%. Consequently only one sample in six was analysed twice in later work.

4.3 Experimental Protocol and Conditions

The experimental protocol was designed so that an initial comprehensive set of experiments on the effect of windspeed and orientation could screen out those samplers that were totally unsuitable.

4.3.1 The effect of windspeed and orientation

Windspeeds in coalmines can vary from less than 0.5 m/s in poorly-ventilated headings to over 6 m/s on some coal faces, and in some main ventilation roadways. Furthermore extensive use is made underground of ventilation ducting for ventilating drivages, headings and other auxiliary ventilation purposes. To investigate whether a particular sampler was universally applicable to underground situations, therefore, experiments were planned to cover a wide range of windspeeds namely 1, 3, 6 and 12 m/s and for two orientations of the sampler - facing the wind (0°), and side-on to the wind (90°).

For each windspeed, six examples of a given type of diffusive sampler were tested simultaneously, three at 0°, and three at 90°. This was normally repeated once to give six samples for each windspeed-orientation combination. Generally each type of sampler was subjected to the above range of tests, but for the SKC 530 and the 3M 3500 samplers a further small set of experiments was carried out where three examples of each type were tested simultaneously with all either at 0°, or all at 90° to the wind. In the statistical analysis of the results (methods described below in Section 4.4) for the main set of runs the 'between-run' factors were sampler type (six types) and windspeed (four values), and the 'within-run' factor was orientation. For the shorter set of runs 'between-run' factors were orientation (0° and 90°) and windspeed (four values), whilst the 'within-run' factor was sampler type.

4.3.2 The effect of turbulent airflows

Airflows underground in coalmines are invariably turbulent with Reynolds numbers typically well in excess of 100,000. In a previous ECSC-funded project (Vincent *et al*, 1983) we demonstrated that turbulent airflows found underground could, to a limited extent, be simulated by the installation into the wind tunnel airflow of square-mesh grids (most of the turbulent structure being produced by the vertical legs of the powered supports). This work also confirmed that the flow behind these grids was stable and the intensity and length scale of the isotropic turbulence produced, could be safely predicted from the dimensions of the grids and the distance downwind from the grids.

For this study four conditions were chosen to cover as wide a range of turbulent values as possible in the small wind tunnel. The conditions given in Table 4.1 included values (in the x-direction) of turbulent intensities in the range 0.06 to 0.20, and turbulent length scales in the range 0.3 to 10.0 cm. Experiments were carried out at a windspeed of 3 m/s, which for an empty wind tunnel gave a Reynolds number of 70,000. For each turbulence condition six examples of a given type of sampler were tested simultaneously; three at orientation 0°, and

three at 90°. With this experimental plan the within-run factor was orientation and the between-run factors were sampler type and turbulence condition.

4.3.3 The effect of vapour loading

Vapour concentrations found underground are likely to be variable in both level and duration. It is important therefore, to ensure that samplers used to measure these vapours display results that are independent of adsorbed vapour load for the range of conditions likely to be found underground. A set of experiments was therefore carried out in which the samplers were exposed to a fixed vapour of 40 ppm for five sampling periods from 60 to 360 minutes; and to concentrations between 40 and 200 ppm for a fixed period of 60 minutes. A further shorter set of experiments was performed with just the SKC 530 and the 3M 3500 samplers which were exposed to a low concentration of 5 ppm for 180 minutes. (See Table 5.14 for experimental plan).

4.3.4 The effect of fluctuating vapour concentrations

When the project was first proposed it was thought that highly fluctuating vapour concentrations, where the amplitude of the pulse was large and the duration of the pulse short in comparison to the rate of diffusion, might be undersampled by diffusive samplers. However, subsequent theoretical and experimental work, mainly by Bartley *et al* (1983, 1987), has shown that providing that the exposure time is long (i.e., eight hour shift) and the appropriate choice of adsorbent material is made, then fluctuations in vapour concentration during the sampling period should have little effect on sampler performance. In the later work a performance test is proposed where the most severe challenge to the performance of diffusive samplers in fluctuating conditions is achieved by using single pulses at both the start and finish of the sampling period rather than a train of pulses as suggested in the earlier literature. A short series of runs was planned therefore in which a 'spike' of vapour of high concentration (~240 ppm) was injected into the wind tunnel for ten minutes at the start of the exposure run. The samplers were then either left in the wind tunnel at zero vapour concentration for a further 470 minutes (to simulate a start pulse), or immediately capped giving a total exposure time of ten minutes (simulating a finish pulse). General procedures for the wind tunnel, as described above, were carried out, and a windspeed of 3 m/s was employed.

4.3.5 The effect of airborne dust

One of the main environmental features found in underground coalmines is the relatively high concentrations of airborne dust. The effect of dust particles depositing on the adsorbent surface or the protective membrane of diffusive samplers has not been widely reported despite the possibility of some effect due to surface blockage.

The collection and retention of dust particles on a vertical surface depends upon both the inertial deposition (where for a given body size collection is a function of the particle aerodynamic diameter (d_{ae}) and the windspeed (U)), and the bounce or blow-off of particles from the exposed surfaces (where particle loss is a function of the particle geometric diameter (d_g) and U). Consequently to cover the range of likely effects, two test dusts were chosen; (a) a near monodisperse fused alumina powder of mass median aerodynamic diameter (mm d_{ae}) = 6 μm, and geometric standard deviatiion (σg) = 1.3; and (b) a polydisperse powder of crushed coal of mm d_{ae} = 30 μm, and σg = 2.0. These were dispersed into the wind tunnel airstream before vapour injection using a rotating table, compressed-air venturi dust feeder. Concentrations of around 20 mg/m^3 for dust A and 300 mg/m^3 for dust B were achieved for two hours whilst a vapour concentration of 40 ppm was injected into the wind tunnel.

4.4 Methods of Statistical Analysis

4.4.1 Response variables analysed

Each of the five series of runs described above was analysed separately, as were the two 'sub-series' of windspeed-orientation runs. Analyses of variance, in which the joint effects of all the experimental factors involved in a series of runs were considered together, were carried out only for the larger set of windspeed-orientation runs and the turbulence runs. For each of the other series of runs, statistical analysis was carried out for each sampler type separately. Of all the experimental factors being considered, only the effects of orientation were examined 'within-run'; comparisons of the effects of all other factors were subject to 'between-run' variation.

The response variable analysed was the same in each of the five series. Consider first those runs involving six devices. Each of these yielded six values of the ratio R, where

$$R = \frac{\text{Vapour concentration by diffusive sampler}}{\text{Vapour concentration by pumped-tube sampler}} \qquad (8)$$

These could be split into two sets of three ratios by the 'within-run' factor, namely orientation. The variable used for analysis was the natural logarithm of the geometric mean of these triplets. For example, if devices at sampling positions 1, 2 and 3 were all placed at orientation 0^0, and those at sampling positions 4, 5 and 6 at orientation 90^0, then a single run of this kind yielded two values of the response variate (Y) namely,

$$Y_0 = \frac{\log R1 + \log R2 + \log R3}{3} \qquad (9)$$

and

$$Y_{90} = \frac{\log R4 + \log R5 + \log R6}{3} \qquad (10)$$

in an obvious notation. Runs involving only three devices yielded only one value of the response variate, namely the logarithm of the geometric mean of the three values of R.

The two analyses of variance, in which sampler type was incorporated as a factor, (strictly the analysis of the windspeed–orientation data should be referred to as an analysis of co–variance, since windspeed was treated as a continuous variable) were complicated by the fact that pairs of responses (Y_0 and Y_{90}) from runs involving six devices were not statistically independent. These analyses were therefore carried out by deriving two further uncorrelated response variables S and D, defined as follows:–

$$S = 0.5\ (Y_0 + Y_{90}) \qquad (11)$$
$$D = 0.5\ (Y_0 - Y_{90}) \qquad (12)$$

Analysis of S yielded significance tests of the effects of 'between–run' factors averaged over sampler; analysis of D yielded tests of the average effect of orientation, and interactions between orientation and the 'between–run' factors.

For those series of runs where the statistical analysis was performed separately for each sampler type, allowance for within–run correlation was not necessary, except in the case of the Perkin Elmer sampler in the vapour loading runs.

4.4.2 Weights used in analyses of variance

In carrying out analyses of variance in which sampler–type was included as an experimental factor, it was necessary to make allowance for the fact that results from some types of diffusive sampler were more variable than others. Analyses were therefore carried out using the method of weighted least squares. Weights corresponding to each diffusive sampler, and specific to each series of runs, were chosen to be inversely proportional to the average within–run variance (see Table 5.1) each one calculated from the three ratios obtained in single runs at a given orientation. The sampler with the largest within–run variance was arbitrarily assigned a weight of unity. The assumption underlying this procedure is that the between–run variance of the responses Y_0 and Y_{90} was proportional to the within–run variance of a single log ratio.

This proportionality also held for the derived responses S and D; it is shown in the Appendix that the between–run variances of these variables were, respectively, $\frac{1}{2}\sigma^2(1+\rho)$ and $\frac{1}{2}\sigma^2(1-\rho)$, where σ^2 denotes the between–run variance of Y_0 and Y_{90} and ρ denotes the correlation coefficient between Y_0 and Y_{90}.

4.4.3 Estimating residual mean squares to be used in the calculation of standard errors

Only in the windspeed–orientation runs were there sufficient 'degrees of freedom for error' to provide a reliable estimate of the between–run variance of the response variables, Y_0 and Y_{90}. In all other series of runs an estimate was derived, from within–run variability of single ratios, by applying a multiplying factor obtained from the analysis of windspeed–orientation data.

In those runs where orientation was included as a within–run factor (other than the windspeed–orientation runs, e.g., turbulence and vapour loading runs), estimates of the residual mean squares to be used in the analyses of variance of S and D were obtained by assuming that the correlation between Y_0 and Y_{90} was of the same magnitude as that estimated from the windspeed–orientation data. Details of the procedures outlined in Sections 4.4.1 – 4.4.3 are given in the Appendix.

5. RESULTS AND STATISTICAL ANALYSIS

5.1 Introduction

Experiments were carried out to investigate the effect on the performances of diffusive samplers of five different 'hostile' environmental conditions. These were: wind velocity and orientation; turbulence; fluctuating concentrations; airborne dust exposure; and vapour loading. Combinations of these various conditions were not tested in this project. All concentrations as measured by the diffusive samplers were calculated using the uptake rates quoted by the manufacturers.

Th conditions considered to be the most crucial to the successful use of diffusive samplers underground were high windspeeds and variable orientations. Consequently these were investigated first with a comprehensive experimental design using all the six types of diffusive sampler. The results were then used to screen out from further investigation some of those samplers whose performance was poor.

5.2 The Effect of Windspeed and Orientation

5.2.1 General

This section contains the detailed account of the results and the statistical analysis, in Sections 5.2.2 and 5.2.3 followed by a summary of the important findings from the results. Some readers may wish, on first reading, to go straight to this summary presented in Section 5.2.4, consulting, if they wish, the data presented graphically in Figures 5.1 to 5.6. Furthermore, as explained in Section 4.3.1, two types of experiments were performed with the windspeed–orientation variables, one where two orientations of a single sampler type were evaluated in each run, and one where two sampler types were evaluated at the orientation in each run. For statistical reasons these are described separately.

5.2.2 Experiments with two sampler orientations evaluated in each run

Results from 35 such runs are summarised in Table 5.1. Each entry in the table represents the geometric mean of three values of the ratio (R), of the vapour concentration measured by diffusive sampler divided by the vapour concentration measured by pumped–tube sampler, all obtained from single experimental runs at a specified windspeed and orientation. The respective geometric standard deviations are given in brackets. The individual values of R themselves are shown plotted against windspeed in Figure 5.1 to 5.6. Also shown are regression lines, fitted by the method of weighted least squares, from which the trends can be seen. On an initial qualitative assessment of the results, one may suggest that the samplers differ considerably from each other regarding their performances in conditions of varying windspeed and orientation.

Specifically, the results from the SKC 530 showed little effect of windspeed and orientation, but measured vapour concentrations were between 30 - 60% higher than those for the corresponding pumped-tube samplers. The 3M 3500 gave results close to those of the pumped-tubes, with no effects of windspeed or orientation. For the MSA OVD device values of the ratio R tended to increase with increasing windspeed, and were somewhat lower at orientation 90° than at orientation 0°. Increasing trends in R with windspeed were also evident for the Drager ORSA 5 and the Dupont PROTEC samplers, whilst for the Perkin Elmer samplers, values of R were low at about 0.45, but with little sign of windspeed or orientation effects.

The statistical significance of these effects was examined in an analysis of variance. To take account of the different amounts of random variation associated with each device, the method of weighted least squares was used. Weights associated with each device were taken to be inversely proportional to within-run variance, and are shown in Table 5.2. The resultant Analysis of Variance tables for S and D (see Section 4.4.1) are given in Tables 5.3 and 5.4 respectively. It is clear from these tables that the effects of windspeed and orientation must be considered jointly, and furthermore, are dependent upon the particular sampler.

A summary of the fitted parameters obtained from the Analysis of Variance is shown in Table 5.5. The two parts of the table, labelled (i) and (ii), correspond to Tables 5.3 and 5.4 respectively, and show intercepts and slopes of regression lines upon windspeed by sampler type. It is important to note here that parts (i) and (ii) do not refer to regressions of Y_0 and Y_{90} (see Equations 9, 10) upon windspeed, but rather to regressions S and D (see Equations 11,12) respectively. The fitted parameters for the actual regression lines are obtained by adding and subtracting the estimates given in Table 5.5 and are given in Table 5.6. These are the lines plotted in Figures 5.1 to 5.6 . Table 5.5 may be interpreted by considering the results for each sampler separately. In general, the slope parameter under (ii) measures the difference between orientations in the linear trend of log R with windspeed, and a statistically significant result here indicates that the pairs of lines in Figure 5.1 to 5.6 are truly non-parallel.

For two devices, the MSA OVD and the Drager ORSA 5, the effects of windspeed upon R depend upon the orientation of the sampler (see Figures 5.3 and 5.4). For the MSA the estimated average increase in R per unit increase in windspeed is 18% at orientation 0°, and 8% at 90°. For the Drager, corresponding figures are 7% and 20%. This dependence can be further demonstrated by showing that for the MSA, at 1 m/s the estimated R at 0° is 1.30 times that at 90°, whilst at 12 m/s the factor is 3.42. Corresponding results for the Drager are 1.11 and 0.30.

Considering now the Dupont PROTEC G-BB, there is no evidence of non-parallelism of the regression lines shown in Figure 5.5, but the statistically significant intercept in Table 5.5(ii) suggests that there is an effect of orientation. At 6 m/s the magnitude of this effect is estimated to be a decrease by a factor of 0.69 in R when measured at 0° compared to that measured at 90°. For the Dupont the effect of windspeed upon R is statistically significant at the 0.01 level, and represents an average increase of 15% per unit increase in windspeed.

No effects of windspeed and/or orientation were found for the Perkin Elmer sampler, the only statistically significant regression parameter being the intercept in column (i). This suggests that the value of R for this device (about 0.46 on average) is genuinely below unity.

For the SKC 530, there is no evidence to support either a differing effect of windspeed at the two orientations 0^0 and 90^0 (i.e., non parallelism) or an effect of orientation (i.e., separate regression lines) upon log R. Also the effect of windspeed averaged over orientation is non-significant ($t = 1.02$, $p > 0.3$), suggesting no overall trend with windspeed. The 't' statistic for the intercept parameter given in Table 5.5(i) is 1.45, which again does not attain significance ($0.15 < p < 0.2$). However, a more appropriate test for elevated values of log R in this case is given by comparing the estimated log R at windspeed 6 m/s to zero. The appropriate value of log R is given by:-

$$0.250 + 6(0.0255) = 0.4030 \quad \text{(i.e., 1.5 in scale of R)}$$

which may be shown to have estimated standard of 0.1045 ($t = 3.86$, $p < 0.002$). At a windspeed in the centre of the chosen range 1 to 12 m/s, there is therefore strong evidence that the SKC 530 device has an elevated value of R.

For the 3M 3500 the evidence suggests that R does not vary from unity for all windspeeds and orientations tested.

Tests for the presence of curvilinearity in the trend of log R with windspeed were statistically non-significant, suggesting that the same model of linear regression used for the statistical analysis was adequate. The clearest evidence of curvilinearity is provided by the Drager device at orientation 90^0. Here the fitted line underestimates R at 1 m/s, and overestimates R at 6 m/s.

5.2.3 Experiments with two sampler types (SKC 530 and 3M 3500) evaluated in each run

This small data set was produced when doubts were expressed over the validity of the initial results with the SKC 530 sampler when the clear bias in performance was first observed. It involves the use of two different types of sampler in the same run where both have the same orientation. For the statistical analysis it was more convenient to analyse data from these runs separately and those findings are presented below.

The results from 11 such runs are given in Table 5.7, where geometric mean values of R together with the respective geometric standard deviations are presented as in Table 5.1. Individual values of R are plotted against windspeed in Figures 5.7 and 5.8. Also shown are the best fit lines by the method of least squares. Values of R for the SKC 530 are appreciably greater than unity (> 1.33) and, at orientation 90^0, were substantially higher at 12 m/sec. For the 3M 3500, R is close to unity for both orientations and all windspeeds.

Tables 5.8 and 5.9 show the analysis of variance for the SKC and 3M devices respectively. Estimated values of parameters (i.e., intercepts and slopes of regression lines of mean log R upon windspeed, by orientation) are shown in Table 5.10. Table 5.8 shows that there is an affect of windspeed upon log R for the SKC device, and that it depends on orientation. These affects are quantified in Table 5.10, (which assumes a linear relationship with windspeed). At orientation 0^0, the slight increasing trend in R with windspeed is not statistically significant but at orientation 90^0 it is significant. Both intercepts are statistically significantly greater than zero, at at least the 5% level, suggesting that the elevation of R at low windspeeds is a real effect.

At orientation 0^0, there is no evidence that R for the 3M device departs from unity. However, at orientation 90^0, there is a significant increasing trend with windspeed ($p < 0.05$) but it is of very low magnitude (0.8% per unit increase in windspeed) and, therefore, unimportant.

The results of this second set of windspeed–orientation runs agree with those in Section 5.1.1 for the 3M device. For the SKC however, there is now a statistically significant increase in the geometric mean value of R with windspeed, at orientation 90^0, probably because of the elevated values at 12 m/s. It can be observed in Figure 5.9 that for the SKC 530 a linear representation of the effects of windspeed may be an oversimplication.

5.2.4 Summary of findings from windspeed–orientation experiments

1. The SKC 530 consistently oversampled, normally by between 25 and 60% at windspeed up to 6 m/sec. At 90^0 to the wind, oversampling was considerably greater and the variability increased.

2. The 3M 3500 was essentially unaffected by variations in windspeed and orientation. The sampler displays very small bias and low variability, with individual values of R ranging from 0.94 to 1.33.

3. The MSA OVD was affected considerably by windspeed and orientation. It had both a large bias and high variability even at low windspeeds. Individual values ranged from 1.26 to 11.77.

4. The Drager ORSA 5 was affected considerably by windspeed and orientation, but at windspeeds up to 3 m/s the bias was not large and the variability relatively low (values of R in these conditions ranged from 0.78 to 1.22). At higher windspeeds the performance deteriorated progressively especially at orientation 90^0 where individual values of R up to 8.91 were observed. Despite these problems tests were continued.

5. The Dupont PROTEC G–BB was affected considerably by both windspeed and orientation. It had both large bias and variability even at low windspeeds. Individual values of R ranged from 1.09 to 12.80.

6. The Perkin Elmer ATD50 was unaffected by variations in windspeed and orientation. This sampler, however, despite displaying low variability had a large consistent bias with values of R ranging from 0.41 to 0.54.

On the basis of these results the 3M 3500, SKC 530, Perkin Elmer ATD50 and the Drager ORSA 5 were investigated in all further tests. The effects turbulence and vapour loading were investigated for the MSA OVD.

5.3 The Effect of Turbulent Airflows

Four different turbulence conditions were studied with experimental design very similar to that used in the windspeed–orientation runs. All runs were performed at a windspeed of 3 m/s with diffusive samplers orientated at 0° and 90° to the wind in each run. Tests were performed with the following 3M 3500, SKC 530, Drager ORSA 5, Perkin Elmer ATD50 and the MSA OVD. Twenty runs in all were carried out.

Table 5.11 shows geometric means and standard deviations of three repeat values of R for each sampler obtained from single experimental runs for each specific turbulence condition. Data from the windspeed–orientation runs (Table 5.1) for the same windspeed of 3 m/s are included in the statistical analysis as a 'no–grid' control. These mean values of R are displayed in Figures 5.9 to 5.13 for each turbulence condition. From these Figures it can be seen that, for the 3M 3500, SKC 530, and Perkin Elmer ATD50, there is little effect of turbulence upon performance. For the Drager ORSA 5, however, R is seen to increase between the 'no–grid' condition and all the four conditions in which turbulence grids were used. There is also a large increase in the random variation of the results for the Drager ORSA 5. The turbulence conditions caused no further deterioration in th performance of the MSA OVD.

Tables 5.12 and 5.13 give the weighted analyses of variance of the derived variables S and D, (see Section 4.4.1). Weights were taken to be inversely proportional to within–run variance. The two degrees of freedom for error in each table were obtained from the windspeed–orientation results for the MSA OVD and the Drager ORSA 5 devices. However, these estimates of error were not used in significance tests. Instead appropriate estimates were obtained using within–run variance in conjunction with results from the windspeed–orientation runs. Details are given in the Appendix. The two Tables show that differences in R between types of sampler are real, and depend on orientation. However differences in R between turbulence conditions for each sampler tested were not statistically significant. This statement includes the Drager ORSA 5 sampler, where random variation in the results did not allow the differences apparent in the Table between turbulent conditions and the no grid control to reach significance. Due to the variability of the results, and the limited amount of data, no systematic relationship between the value of R and any function embodying the turbulent mixing caused by the grids was found.

5.4 The Effect of Vapour Loading

The effects of vapour loading were investigated for five types of diffusive samples (SKC 530, 3M 3500, Drager ORSA 5, Perkin Elmer ATD50 and the MSA OVD). All samplers were positioned facing the wind, but with the Perkin Elmer ATD50, three samplers were positioned facing the wind and three side-on during each run. A total of 15 runs was carried out.

Table 5.14 shows geometric means and standard deviations of three values of R, all obtained in single experimental runs, carried out under the specified experimental conditions. The results suggest that there is very little effect on R of varying vapour concentration, loading or time, with two exceptions, the high result for the SKC 530 at a concentration of 5 ppm, and the comparatively low result at 100 ppm for the MSA OVD. For statistical analysis, data from the windspeed-orientation runs for the same windspeed of 3 m/s are included as one of the exposure conditions. This gave 23 runs in total. The complexity of the data structure was such that the results from each device were analysed separately.

A one-way analysis of variance was carried out for each of the SKC 530, 3M 3500, MSA OVD and Drager ORSA 5. For this purpose runs of 60, 80 and 90 minutes were considered together as of 'short' duration, giving six experimental conditions to be compared in each analysis of variance. For the Perkin Elmer ATD50, two analyses of variance of variables S and D were carried out, since two orientations were examined in each run. Although an estimate of residual variability was available for the SKC 530, 3M 3500, MSA OVD and the Drager ORSA 5 devices (with low degrees of freedom), significance tests were performed using estimates of error obtained from the within-run variation, as in the analysis of the turbulence runs. Details are given in the Appendix.

The analyses of variance are given in Table 5.15(a) and (b). There is evidence of differences in R between experimental conditions for the SKC 530. Comparisons of the geometric mean values of R showed that the significant variance ratio was due to the high result at the vapour concentration of 5 ppm; none of the ratios obtained at other conditions differed significantly. This low concentration of 5 ppm was unfortunately not evaluated for any of the other devices, and there was no evidence of a statistically significant vapour loading effect for the other conditions tested. The two analyses of variance carried out for the Perkin Elmer ATD50 showed no significant effect of vapour loading but a possible small effect, over all loadings, of orientation ($0.1 < p < 0.25$), mean values of R at 90^0 (0.45) being slightly lower than at 0^0 (0.48) - see Table 5.14.

5.5 The Effect of an Intitial Vapour Spike

As explained in Section 4.3.4, the effect of continually fluctuating vapour concentrations during the exposure period had been demonstrated by other workers to be minimal. However, the degree of retention of vapour molecules sampled by the diffusive sampler, from a large initial spike of vapour, when it was followed

by a period of zero exposure still remained open to the question. Eight runs were carried out therefore, to investigate the problem with four types of diffusive sampler, (SKC 530, 3M 3500, Perkin Elmer ATD50 and Drager ORSA 5).

Table 5.16 shows geometric means and standard deviation of three repeat values of R obtained in single experimental runs carried out under the specified conditions. Data from five windspeed–orientation runs are also shown; these are included in the statistical analysis as 'steady–state' controls. It is clear from inspection that there are no statistically significant differences between values of R obtained under the three experimental conditions for the 3M 3500 and the Drager ORSA 5. A t–test of the difference between the average 'spike–run' result and the control for the SKC 530 was significant at the 1% level suggesting that the increase in R might be a real effect. For this test, an estimate of between–run variability, obtained from the observed within–run variability, was used. The observed decrease in R at run time 480 minutes for the Perkin Elmer ATD 50 was not statistically significant.

5.6 The Effect of Exposure to Airborne Dust

A short series of runs was performed to investigate the effect of airborne dust on the performance of diffusive samplers. Three runs were carried out for each of two test dusts dispersed into the wind tunnel with nominal dust concentrations of 21 ± 0.5 mg/m^3 for the fine, monodisperse aloxite dust and 87 ± 13 mg/m^3 for the polydisperse coal dust (see Section 4.3.5 for details of particle size). Four types of diffusive sampler were evaluated (SKC 530, 3M 3500, Drager ORSA 5 and Perkin Elmer ATD50) at a constant windspeed of 3 m/s, and orientation 0^0 , for a constant exposure period of 120 mins for dust A and 360 mins for dust B.

Table 5.17 gives geometric means and standard deviations of sets of three values of R for each type of diffusive sampler, and these are also displayed in Figure 5.11. By inspection there is clearly no difference in R between the two types of dust for both the 3M 3500 and the Perkin Elmer ATD50. For the SKC 530, a small difference in R (mean values 1.42 and 1.34) was observed, but a t–test showed that this difference failed to reach significance ($0.2 < p < 0.3$). For the Drager ORSA 5 there was also a small difference in the mean values of R for the two types of dust (1.05 and 0.97), but in this case it was significant ($p < 0.01$). (Here, as before, the estimated standard errors used in the 't' tests were obtained from within–run variance in conjunction with results from the windspeed–orientation runs). Unfortunately for this data set it was not possible to include rigorously the 'no–dust' results from Table 5.1 because no runs were performed in that series at a windspeed of 2 m/s. Nevertheless it is instructive to compare on an informal basis the results presented here with those at 3 m/s in Table 5.1. It can be seen that for all four types of sampler there is little effect on the values of R by the presence of airborne dust.

6. UNDERGROUND INVESTIGATIONS

6.1 Introduction

It is essential in any sampler investigation to include a field trials phase in the work programme to support the conclusions drawn from the laboratory studies. The work presented here described a limited trial carried out underground to monitor toluene vapour released during the joining of a steel-cord conveyor belt. As the use of organic solvent is not centrally monitored, suitable sites where 1,1,1 trichloroethane was being used in sufficient quantities were difficult to find. British Coal approval procedure for the joining of steel-cord belts specify that monitoring of vapour should take place during the operations.

6.2 Experimental Method

The colliery chosen is situated in the northern part of the Nottinghamshire coalfield. The investigations took place in the return roadway cross-cut just downwind of a main belt transfer point. The coalface was ventilated homotropally and consequently the return roadway was used to convey the coal away from the coalface. A sketch of the site is given in Figure 6.1.

The work being monitored concerned the extension of the main steel-cord conveyor belt by the addition of 50 m of new belting. This process involved two joining (or splicing) operations in which the ends to be joined were prepared by stripping away (with sharp knives) the rubber from the stranded steel cords, which were cut according to a special pattern. Once free from rubber, the cords were then cleaned with toluene, painted with cable primer and coated with rubber cement. The two ends were then placed together on thin rubber sheeting, the gaps filled with rubber strip, a second rubber sheet placed on top, and the joint cured by heating between copper plattens for approximately two hours.

Monitoring was carried out during cleaning and cementing since most of the toluene would be released during this period. The instrumentation comprised four sampling sets (shown in Figure 6.2) centred around Casella type AFC123 intrinsically-safe sampling pumps. Each pump provided the suction for between 2 - 4 pumped-tube reference samplers, and also carried (on a special bracket) one example of each of the four types of diffusive samplers: SKC 530, 3M 3500, Drager ORSA 5 and Perkin Elmer ATD50.

The four pumps were sited on a platform positioned across the conveyor structure some 3 m downwind of the joining area, and at the same height as the belt ends, as shown in Figure 6.1. For each pump the relative positions of each type of diffusive sampler was varied in an attempt to minimise bias due to vapour concentration gradients. High capacity (SKC Sorbent) pumped tubes were used as reference samplers, the flowrates through which were checked at the start and end of the sampling period using a calibrated rotameter. The diffusive samplers were equipped with protective sealing caps which were removed at the start of the

sampling period (when the pumps were switched on) and replaced as quickly as possible at the end. All the samplers, both pumped-tube and diffusive were positioned with their entries facing into the wind (orientation 0°). The mean windspeed in the centre portion of the roadway (close to the conveyor belt) was 2 m/s, giving a Reynold's number for the bulk flow in the roadway of approximately 500,000.

The entire process took place over the Easter weekend (1989) so that coal production would not be affected. The belt jointing process lasted two hours. This meant, therefore, that airborne dust levels would be very low. Owing to logistic problems the vapour released from only one of the two joints was monitored. However, a second sample was obtained by simulating the cleaning process using an equivalent quantity of toluene.

Analysis of the various samples for toluene was carried out in the main IOM laboratory using same procedures described in Section 4.2 except that Analar grade toluene was used for calibration. In the light of the laboratory studies, the uptake rates used to calculate the mass of vapour collected by each sampler for toluene were determined by exposure in the wind tunnel at a windspeed of 1 m/s. These are given in Table 6.1 and are discussed later.

6.3 Statistical Methods

The data formed as a three-way cross classification, with classifying factors, run number (two runs), sampling station (four stations) and sampler type (five types - four diffusives and a pumped tube). There was one observation in each 'cell' of the classification, which gave 40 observations in total.

An analysis of variance was carried out on the log-transformed data, run number and sampling station being regarded as random factors. Differences between samplers were tested by an 'F' test, using the 'interaction' terms between samplers and runs as residual (see Table 6.2). Individual contrasts between samplers were tested using one quarter of the 'interaction' term as an estimate of the variance of the contrast.

6.4 Results and Comments

The results obtained with the various samplers are given in Table 6.2. Mean values of vapour concentration (in ppm) are presented for the pumped-tube samplers and the four types of diffusive sampler at each sampling station. From the pumped-tube data it can be seen that, although there is a 2:1 difference in overall vapour levels between the two runs, the concentration profiles are identical, there being a slight increase from the side to the centre of the roadway. This means that it is valid to assess the two runs as repeats under esentially unchanged conditions.

All four types of diffusive sampler gave results that were higher than those for the pumped-tube samplers, with both the SKC 530 and the Perkin Elmer ATD50 having mean values of R of 1.15, and the 3M 3500 and the Drager ORSA 5 values of 1.11 and 1.05 respectively. The analysis of variance (carried out on logged data) is shown in Table 6.3. Since the four sampling stations and the two repeat runs were both treated as random samples from hypothetical populations of stations and runs respectively, consideration of expected mean squares showed that there was no immediate 'F' test of significance of differences between samplers. However, the analysis suggested that it was reasonable to assume that average differences between samplers were not dependent upon sampler position (i.e., that the 'SxP' effect is zero. An 'F' test for sampler differences was then available using the mean square value for 'SxR' in the analysis of variance table. This suggested that the differences between the five types of sampler were too great to be attributable to chance ($p \sim 0.1$). It may be shown that the estimated standard error of the difference between any pair of mean values (on the log scale) is 0.0416. A t-test (4 degrees of freedom) showed that the observed biases of 1.14 and 1.15 for the SKC and Perkin-Elmer devices respectively relative to the pumped tube were statistically significant at the 0.05 level. The bias for the 3M device (1.11) was not quite statistically significant ($0.05 < p < 0.1$). All other differences between pairs of samplers were not statistically significant.

The results of the field exercise are fully compatible with the earlier laboratory trials. If the manufacturer's uptake rates (Table 6.1) had been used the results from the Perkin Elmer ATD 50 would have been very substantially lower than the pumped NIOSH tube method and those from the SKC 530 substantially higher. As the ventilation in the roadway was 2 m/s the performance of the Drager ORSA 5 was much as expected from the laboratory trials. The reasons for the apparent oversampling by all the diffusive samplers are difficult to ascertain. Small systematic errors in the determination of the uptake rates, analytical procedures and the pumped sampler flow rates could all have contributed.

It is also possible to make some observations concerning the occupational hygiene aspects of the process. The British Coal Acceptance specifies that solvent vapours shall be kept to acceptable levels during use. Measurements taken during the cleaning and cementing processes (run 1) with vapour samplers positioned some 3 m downwind gave average levels of toluene of 28.0 ppm. The operational exposure limit (OEL) for toluene is 100 ppm for an eight hour working shift. A level of 28 ppm for two hours represents a full-shift exposure of 7 ppm - well below the OEL. Whilst these levels are low, one observation deserves mention. During the cleaning and cementing process two teams of two men were involved simultaneously on each end of the joint. Obviously one team would be exposed not only to vapour generated by their own actions but also that generated by the team upwind. Concentration of effort on to one end of the belt at a time would overcome this potential problem.

7. DISCUSSION

The main message from the results of this project is that only one sampler – the 3M 3500 – performed according to its specification under the conditions tested in the laboratory and the field.

The Perkin Elmer ATD50 and the SKC 530 should only be used if the uptake rates for the specific chemicals sampled have been determined experimentally. The manufacturer's quoted uptake rates were substantially different from those determined in the laboratory.

The Drager ORSA 5 can only be used effectively in those locations in coalmines where windspeeds and turbulence levels are low. As other more suitable devices are available we would not recommend the ORSA 5 for coalmine use.

Both the MSA OVD and the Dupont Protec G-BB gave results with too large a variability and dependence upon windspeed to be of use in most workplaces.

For diffusive samplers to be of use generally, the uptake rates for each chemical quoted by the manufacturer must be applicable in practice. Of the four usable devices the quoted uptake rates for two did not hold even in relatively low windspeeds (Table 7.1). At windspeeds of only 1 m/s both 1,1,1 trichloroethane and toluene were sampled by SKC 530 at a rate substantially higher (ca 40%) than quoted by the manufacturer whereas the Perkin Elmer ATD 50 sampled at around half the quoted rate. This means that results obtained with the SKC 530 or the Perkin Elmer ATD50 in atmospheres containing vapours of 1,1,1 trichloroethane or toluene, or perhaps other vapours, would be significantly in error if the manufacturers uptake rates were used.

This particular problem with the use of diffusive samplers is very worrying and needs to be resolved. Consequently, the manufacturers and suppliers of those devices where the quoted uptake rates produce values of R appreciably different from unity were informed. Various explanations were discussed and diffusion barriers and membranes appear to be critical factors. A central library of validated uptake rates, that are updated frequently and readily accessible, would help the user overcome problems with uptake rates published by manufacturers. The Health and Safety Executive in Britain has just released this information in its EH40 database (HSE 1990).

In the laboratory tests to investigate how aerodynamic parameters (windspeed-orientation, turbulence) affect performance, an appreciable degree of variability was found. For use in coalmines and other locations where windspeeds could be high (e.g., in the ambient atmosphere) it is essential that the performance of a diffusive sampler is independent of windspeed effects but most designers of diffusive samplers only take account of the effect of concentration depletion at very low windspeeds (< 20 cm/s). From consideration of the mechanisms involved however, it can be shown that in the absence of any diffusional resistance between the external vapour concentration and the internal adsorber then the mass transfer

equation will apply and the diffusional mass flux (M) produced will be dependent upon external windspeed, i.e.,

$$M = k A C \qquad (13)$$

where k is the convective mass transfer coefficient (which is velocity dependent), and A is the cross-sectional area of the adsorber. The developers of the first viable diffusive sampler Palmes and Gunnison, 1973) appreciated this problem and chose to introduce an internal diffusional resistance that controlled the sampling rate. This they achieved by placing the adsorber at the closed end of a cylindrical sampling tube whose length to diameter ratio (L/d), which provides diffusion resistance, is large.

This is the principle of the design of the Perkin Elmer ATD50, which has a diffusion length of 15 mm and internal diameter of 5 mm, and we have shown that its performance is independent of windspeed from 1 to 12 m/s. This sampler, described by Brown *et al* (1981), also incorporates a stainless steel gauze and silicon membrane at the sampler entry to assist in minimising the effects of external winds. The membrane is also employed to minimise the ingress of aerosol particles, which it achieves successfully, although as discussed above, the uptake rate of the device is considerably yet consistently reduced by its presence. Some loss of trichloroethane was observed in the studies of the effect of spikes of concentration. The adsorbent used in the study was Tenax and the problem of sample loss may be somewhat reduced if a different adsorbing medium, e.g. Chromosorb 102, were selected. A range of porous polymer adsorbents is suitable for use in the ATD50 samplers and care must be taken to ensure that the adsorbent/analyte combination is compatible

This principle is also employed (in a modified form) in the design of the Dupont PROTEC G-BB. This sampler uses a diffusion barrier, placed over the adsorber, that has 281 cylindrical holes, each with L/d greater than 3. The designers (Lautenberger *et al*, 1980) predicted that this will be sufficient to prevent the adverse effects of external winds. Our results however, as shown in Table 5.1, do not support this prediction. It performed poorly with high variability displayed even at a windspeed of 1 m/s. This finding is in direct conflict with Lautenberger's results. To confirm that this effect was indeed due to aerodynamic processes a short series of supplementary experiments was carried out with various membranes, including those from the 3M 3500 and MSA samplers and cellulose ester filters, placed over the multihole diffusion barrier. The ratio R was determined for windspeeds of 1, 6, 12 m/s, and orientation 0^{0}, using experimental procedures as described above. The results depended on which membrane(s) were used but an appreciable improvement in performance was seen, with both the mean value and the variability of R being reduced at all windspeeds with all membranes and membrane combinations tested. There was no systematic attempt to identify the best membrane or test a range of membrane types. Nevertheless this limited study suggests aerodynamic processes caused the poor performance and development work on a suitable membrane windshield might improve performance to an acceptable level.

The Drager ORSA 5 sampler again uses a cylindrical tube to house adsorbent material, but in this case both ends of the tube are open and the adsorber is held in place by two cellulose acetate porous plugs. Pannwitz (1986), when describing the sampler, stated that the plugs were designed to control the sampling rate by providing a resistive barrier to diffusion. He presented results that showed very little effect on performance for windspeeds up to 2.5 m/s. Whilst our results show reasonable performance up to 3 m/s, at higher windspeeds R increased strongly with windspeed, especially when the sampler is oriented at 90° to the wind. In this orientation the axis of the tube itself is in line with the direction of the airflow. The tube can then be considered as a bluff body with positive pressure at the front end and negative pressure in the wake formed at the rear end. Because the tube is open at both ends, it is suggested that convection takes place down the tube and vapour no longer reaches the adsorber solely by diffusion. Obviously with this mechanism, the convected contribution to the adsorbed vapour increases as the windspeed increases and progressive oversampling occurs. A similar effect could possibly explain the high values of R for this sampler when subjected to turbulent airflow conditions. The results in Table 5.11 show a substantial increase in both the mean values and the variability of R. Penetration of the cellulose acetate foam diffusion barrier by turbulent eddies, carrying vapour molecules, could be a possible mechanism here. One simple method to minimise the convection of vapour through the tube to the adsorber may be to cap one end of the tube but a lower sampling rate would result. There were some quality control problems with this sampler as the first batch of samplers supplied was contaminated during manufacture or supply by 1,1,1 trichloroethane. This device is, of course, primarily intended as a personal sampler and these effects may be much less when they are worn as such because of the protection offered by the wearer's body. A short laboratory investigation could readily be carried out to ascertain whether harsh conditions would pose problems if the ORSA 5 were used, as intended, as a personal sampler.

The remaining three types of sampler are all 'badge-type' with diffusion barriers supposedly defining the sampling rates of vapour molecules collected by adsorbent material of relatively large surface area.

We believe that the poor performance of the MSA OVD sampler could be associated with the design of its diffusion barrier. In this sampler, a paper windshield rests on top of the charcoal cloth adsorber and is held in place by a plastic cover (see Figure 3.3). On inspection of the sampler we found that the windshield was not held tightly by the cover plate and flapped in the wind, thus possibly allowing leakage of vapour molecules to occur at the edges of the wind shield. This leakage would probably not occur at the low windspeeds at which the performance of diffusive samplers are normally evaluated, but should be solvable with some further development on the design of the wind shield.

The performance of the 3M 3500 sampler was unaffected by all the environmental conditions tested, but it is suggested that care must be taken to avoid gross contamination due to the accidental splashing of solvent onto the membrane. Areas where solvent spraying is carried out may not be suitable. Care also must be taken to avoid accidental physical damage to the membrane whose large surface area could be particularly vulnerable underground. The inclusion of some form of

wire mesh or plastic shield would protect the sampler.

The SKC sampler was also largely unaffected by the environmental conditions tested although it should be remembered that the quoted uptake rates appear high. As a badge sampler, it too is quite liable to splashing and it would be subject to the same restrictions in use as the 3M 3500.

8. CONCLUSIONS

The results of the research have clearly demonstrated that diffusive sampling could be used successfully to monitor toxic gases and vapours in the harsh environmental conditions which prevail in coalmines and that diffusive samplers are potentially flexible, simple and cheap tools for this purpose.

There are difficulties. In tests with only two vapours, just one sampler of the six tested (the 3M 3500) performed to its specification. (This device, we believe, is the most suitable for coalmine use). One did not perform as a static sampler in harsh conditions, two required recalibration and two were totally unsatisfactory. Table 8.1 summarises the performances of the six samplers tested. It is therefore essential that, before a diffusive sampler is used to measure any gas or vapour, independent validation data are obtained.

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APPENDIX 1

Statistical Methods

A1.1 Introduction

This Appendix contains a broad description of methods used in the analysis of the five series of experimental runs. Sections A1.2 to A1.6 give details for each series.

Analyses of variance, in which the type of diffusive sampler under consideration was included as an experimental factor, were carried out on data from only two of the five series – the larger set of 'windspeed orientation' runs and 'turbulence' runs. In these two series the method of weighted least squares was used, to allow for the fact that each device had associated with it different degrees of between-run random variation. In fact, the need for a weighted analysis was inferred from the observed differences between samplers in within-run variation rather than between-run. This was because direct measures of between-run variation, although available for each sampler except the SKC 530 in these two series, could only be based on small numbers of repeat measurements.

The fundamental assumption was therefore made, that for each device, the between-run variance of log R meaned over three determinations within run (see Section 4.4.1 of the main Report), was proportional to the within-run variance of a single determination of log R. The proportionality factor was assumed to be the same for each sampler, and in each series of experimental runs. Under this assumption, weights used in analyses of variance were set to be inversely proportional to average within-run variances of log R for each sampler.

Tests of significance for the larger set of windspeed orientation runs did utilise a 'pooled' measure of between-run variation, obtained from the analysis of variance (see Tables 5.3 and 5.4). This quantity gave an estimate of between-run variance for the device with the greatest within-run variability (which had been arbitrarily assigned a weight of unity). However, for turbulence runs, no such measure was available, and an estimate was obtained from within-run variation, assuming proportionality. The multiplying factor was obtained from windspeed orientation data.

Data from all other series of runs (i.e., the smaller set of windspeed orientation runs, vapour loading runs, 'spike' runs, and dust runs) were analysed separately, by sampler type, and weighting was not used. Measures of between-run variability were obtained from within-run variability, using the proportionality factor derived from windspeed orientation data, exactly as in the case of turbulence data.

A1.2 Windspeed–orientation: Large Series of Runs

The 35 runs provided 70 estimates of within–run variability. These are summarised by sampler type in Table 5.2 of the main report. The most variable sampler was the Dupont, which was assigned an arbitrary weight of unity. The weights for the other devices are also shown in the Table.

These weights were assumed to be inversely proportional to the between–run variances associated with the quantities Y_0 Y_{90}, introduced in Section 4 of the Report. They also apply to the derived variables S and D, since:

$$\text{Variance (S)} = \text{Variance } ((Y_0 + Y_{90})/2)$$

$$= (\text{Variance } (Y_0) + 2 \text{ Covariance } (Y_0, Y_{90}) + \text{Variance } (Y_{90}))/4$$

$$= \tfrac{1}{2} \sigma^2 (1 + \rho)$$

where σ^2 denotes the between–run variance of Y_0 and Y_{90} (for the Dupont, in this case) and ρ denotes the correlation coefficient between Y_0 and Y_{90}. Similarly,

$$\text{Variance (D)} = \tfrac{1}{2} \sigma^2 (1 - \rho)$$

In the analysis of other series of runs, it was necessary to use an estimate of ρ. This was obtained from the residual mean squares from the analyses of variance of S and D (MS(S) and MS(D), say) as follows:

MS(S) estimates $\tfrac{1}{2} \sigma^2 (1 + \rho)$

MS(D) estimates $\tfrac{1}{2} \sigma^2 (1 - \rho)$

Hence,

MS(S) + MS(D) estimates σ^2

MS(S) – MS(D) estimates $\rho \sigma^2$

Substituting the results from Tables 5.3 and 5.4 gives

estimated $\sigma^2 = 0.1293 + 0.0337 = 0.1630$,

estimated $\rho \sigma^2 = 0.0956$,

and therefore,

estimated $\rho = 0.5865$

The factor relating average 'within–run' variability to 'between–run' variability was also used in later analyses. From Table 5.2, the within–run variance of the

Dupont is 0.09335, and hence the multiplier by which the between-run variance is obtained from the within-run variance is

$$0.1630/0.09335 = 1.7461$$

A1.3 Turbulence Runs

The average within-run variances, by sampler type, are shown in Table A1.1. (Data from windspeed-orientation runs for windspeed 3 m/s are also included, as a 'no turbulence' control). The most variable sampler is the Drager, and this device was arbitrarily assigned a weight of unity in the analysis of variance.

As estimate of between-run variability is given by

$$(1.7461)\ (0.1786) = 0.3119$$

and this quantity was assumed to have 23 degrees of freedom, for the purposes of significance tests (see Tables 5.3 and 5.4). Assuming a within-run correlation of 0.5865, the estimated residual mean squares appropriate to the analysis of variance of S and D are, respectively,

$$\tfrac{1}{2}\ 0.3119\ (1 + 0.5865) = 0.2474$$

$$\tfrac{1}{2}\ 0.3119\ (1 - 0.5865) = 0.0645$$

A1.4 Vapour Loading Runs

Table A1.2 shows the average within-run variances, by sampler type, together with the estimated between-run variances obtained by applying the factor 1.7461. These estimates were used in significance tests (see footnote to Table 5.15(a). In runs involving the Perkin-Elmer device, orientation was included as a within-run factor, and the appropriate residual mean squares for the analysis of derived responses S and D were

$$\tfrac{1}{2}\ 0.007325\ (1 + 0.5865) = 0.005811,$$

and

$$\tfrac{1}{2}\ 0.007325\ (1 - 0.5865) = 0.001515,$$

respectively. These were assumed to have 20 degrees of freedom, i.e., the number of triplets of ratios multiplied by two degrees of freedom from each triplet.

A1.5 'Spike' Runs

The average within-run variance of log R for the SKC device was 0.000303, and multiplication by the factor 1.7461 gave an estimate of 0.000528 for the between-run variance of the mean of three determinations of log R. The estimated standard error of the comparison between 'spike' runs and steady concentration control runs was therefore given by

$$\text{Square root } (0.000528\ (1 + \tfrac{1}{3})) = 0.0282$$

In the t-test using this quantity, six degrees of freedom were assumed - two from each triplet of ratios obtained from each run.

A1.6 Dust Runs

Significance tests were carried out only for the SKC and Drager devices. The average within-run variances of log R were 0.000585 and 0.000041 respectively. Estimated between-run variances of the mean of three such log ratios were therefore 0.001021 and 0.000072, and estimated standard errors of differences in such means between dust types were 0.0452 and 0.012 for the two devices. In t-tests, four degrees of freedom were assumed for the standard errors of differences.

Table A1.1

Turbulence data (two orientations examined in each of 20 runs. Seven additional runs included from windspeed–orientation data)

Average variances of log ratio (diffusive ÷ pump), within run and at a constant orientation, by diffusive sampler type, with weighting factor used in analysis of variance.

Sampler	No. of triplets of ratios	Average 'within triplet'variance	Weight
SKC 530	10	0.00484	37
3M 3500	10	0.00155	115
MSA	12	0.02401	7
Drager	12	0.17857	1
Perkin Elmer	10	0.00520	34

Table A1.2

Concentration–time data

Average variances of log ratio (diffusive ÷ pump), taken over sets of three ratios obtained from single runs on specific samplers at constant orientation

Sampler type	No.of triplets of ratios	Average 'within triplet' variance	Estimated between-run variance of means of three log ratios
SKC 530	7	0.00843	0.0147
3M 3500	8	0.00463	0.0081
MSA	6	0.03686	0.0644
Drager	6	0.00488	0.0085
Perkin Elmer	10	0.00420	0.0073

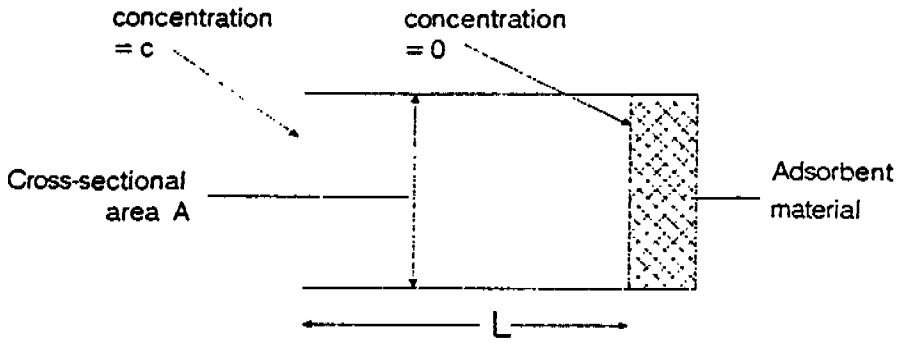


Figure 1.1 Schematic diagram of tube-type diffusive sampler

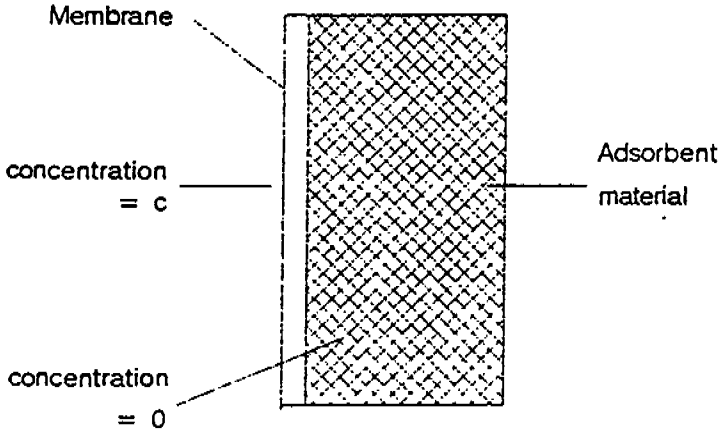
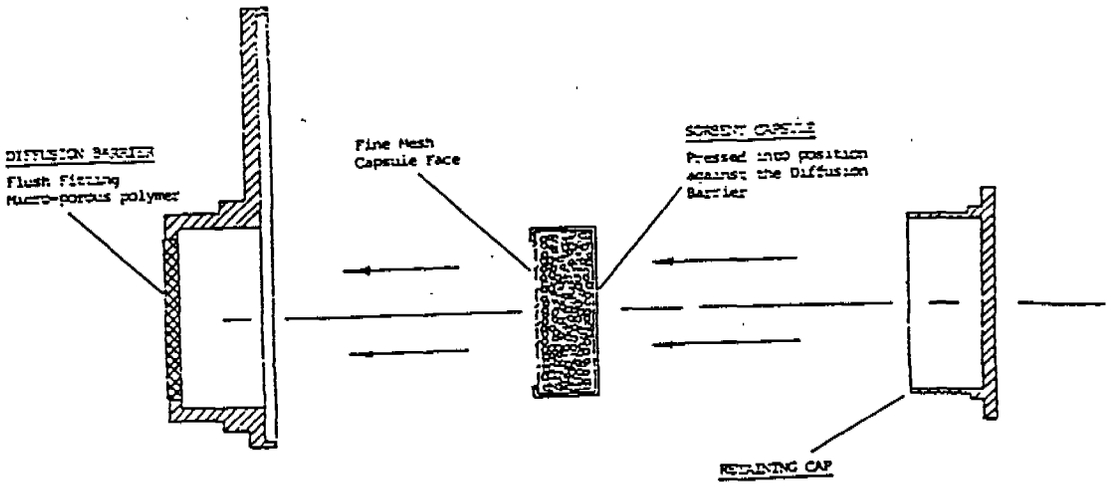
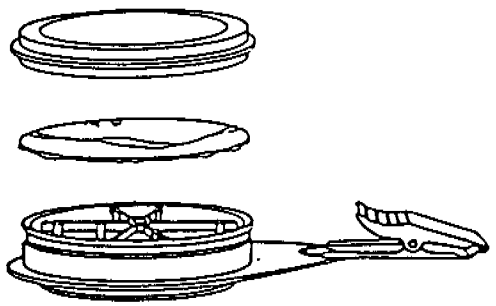


Figure 1.2 Schematic diagram of permeation-type diffusive sampler



Sectional View of Diffusion Geometry.

Figure 3.1 The SKC 530 Diffusive Sampler



This compact design containing a single charcoal sorbent provides an economical way to obtain accurate and reliable exposure readings. Analysis of the single sorbent saves on laboratory costs. In addition, the elimination of sorbent transfer or handling improves accuracy.

Figure 3.2 The 3M 3500 Organic Vapour Monitor

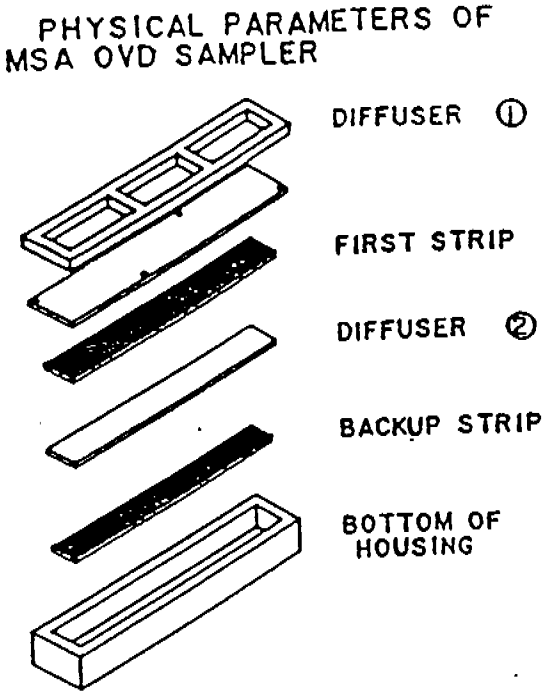


Figure 3.3 The MSA Organic Vapour Dosimeter (OVD)

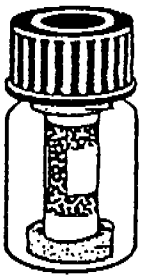


Fig. 1
ORSA 5 sampling tube packed for transportation

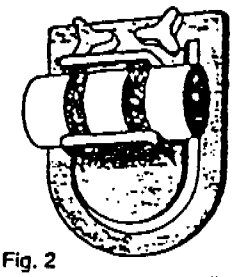


Fig. 2
ORSA 5 during sampling

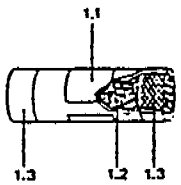


Fig. 3
Design of sampling tube

Fig. 3
1.1 Writing surface
1.2 Adsorption layer, consisting of approx. 400 mg of coconut shell carbon (grain size 0.4...0.8 mm)
1.3 Diffusion sections (acetate cellulose)

Figure 3.4 The Drager ORSA5 Diffusive Sampler

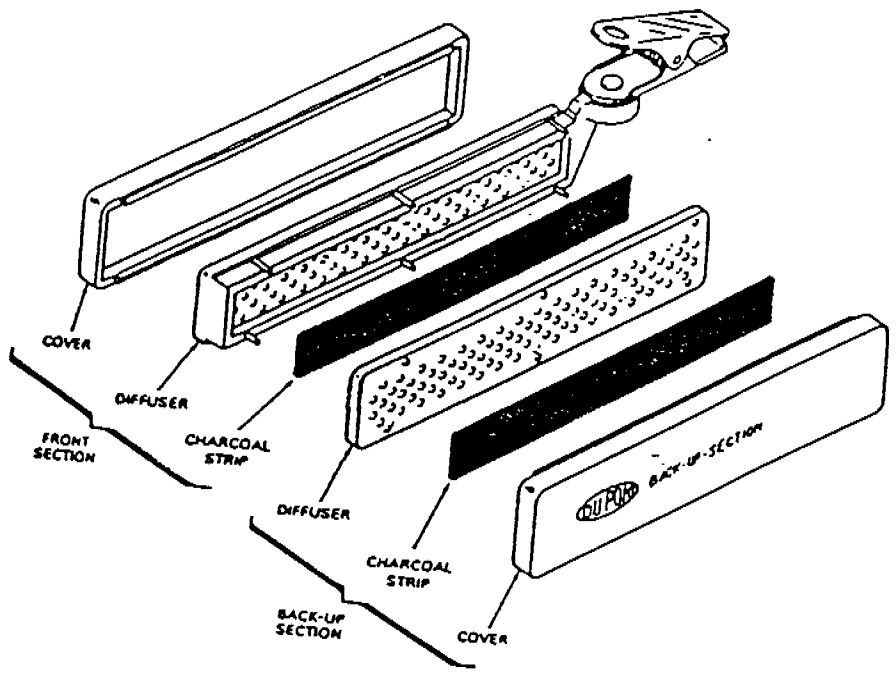


Figure 3.5 The Dupont PROTEC G-BB Diffusive Sampler

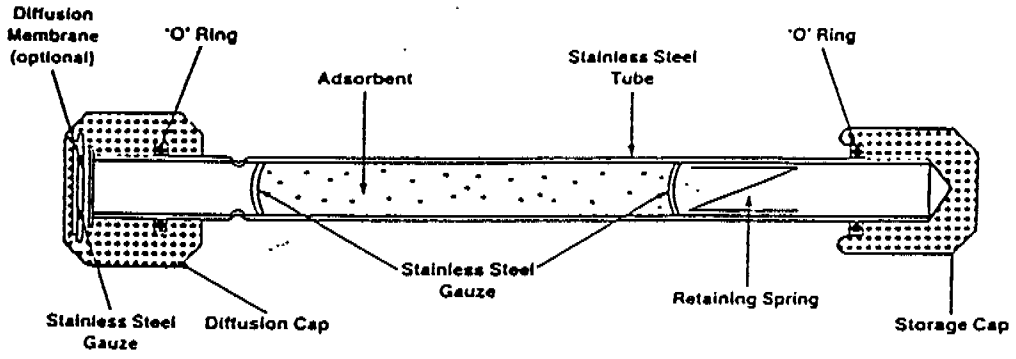


Figure 3.6 The Perkin Elmer ATD50 Diffusive Sampler

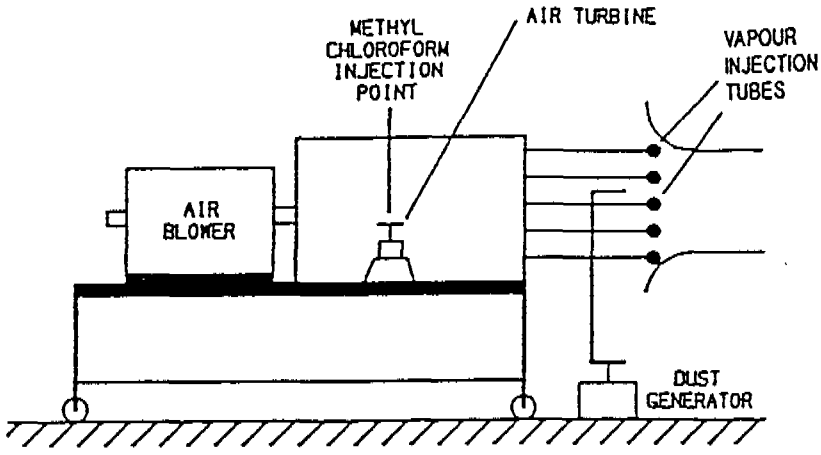


Figure 4.2 Vapour Generation System

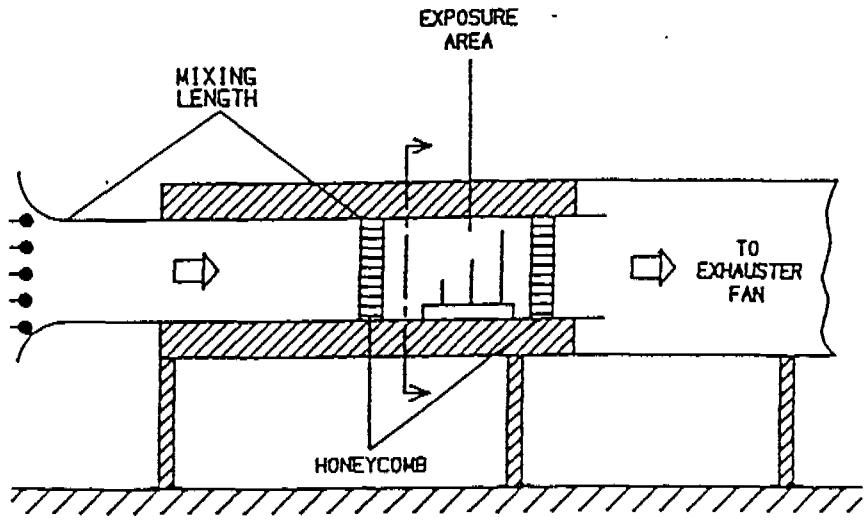


Figure 4.1 Exposure Chamber

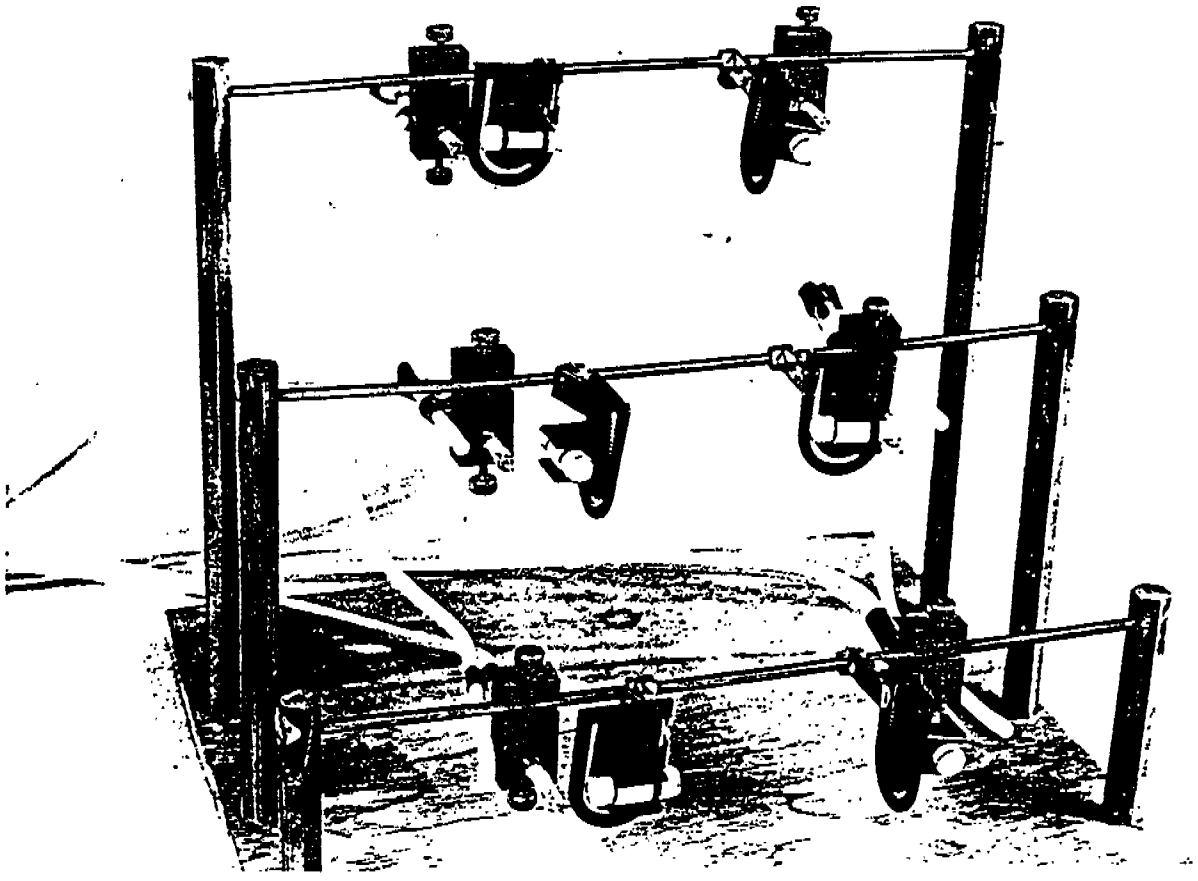
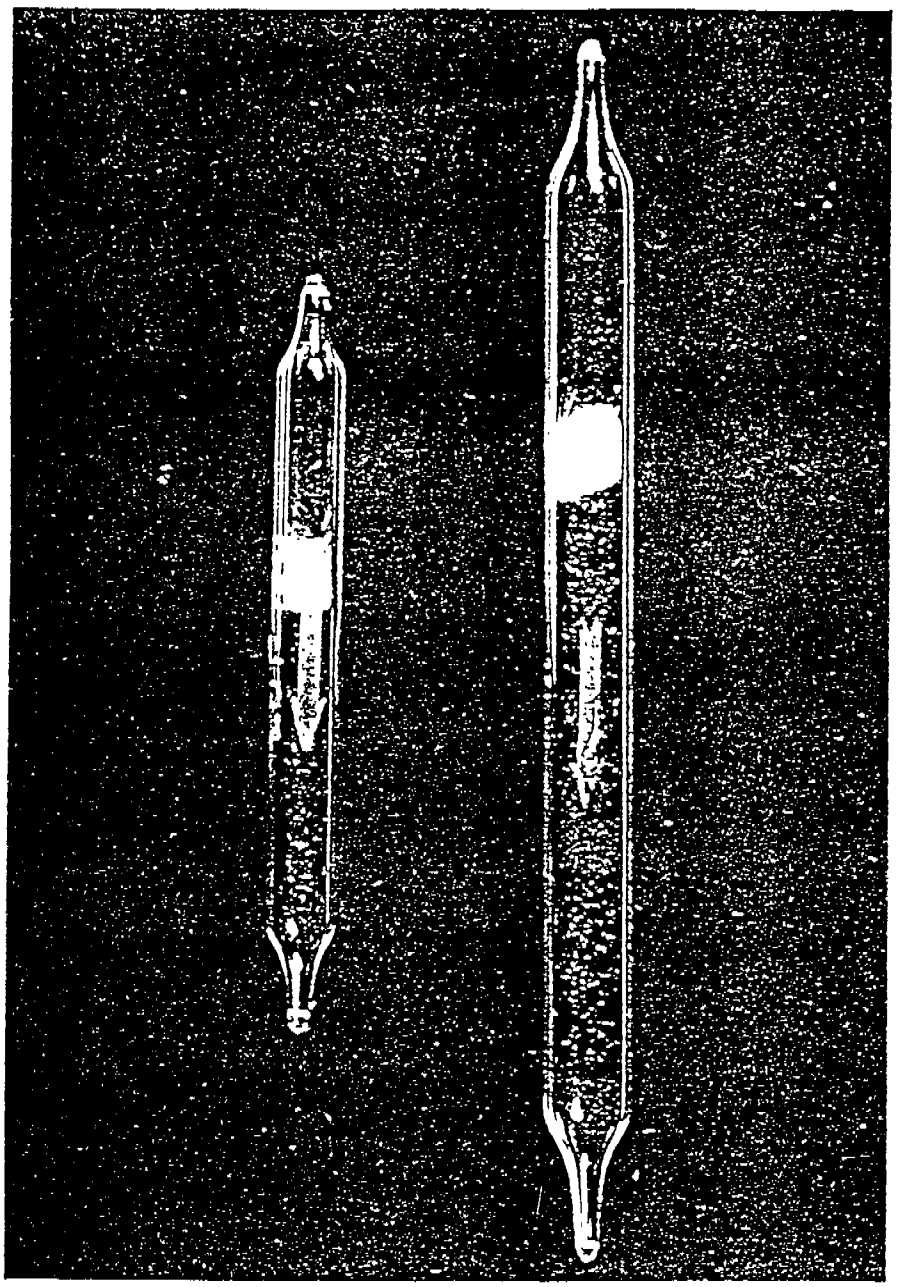


Figure 4.3 Arrangement for holding Diffusive and Pumped-tube Samplers in Exposure Chamber



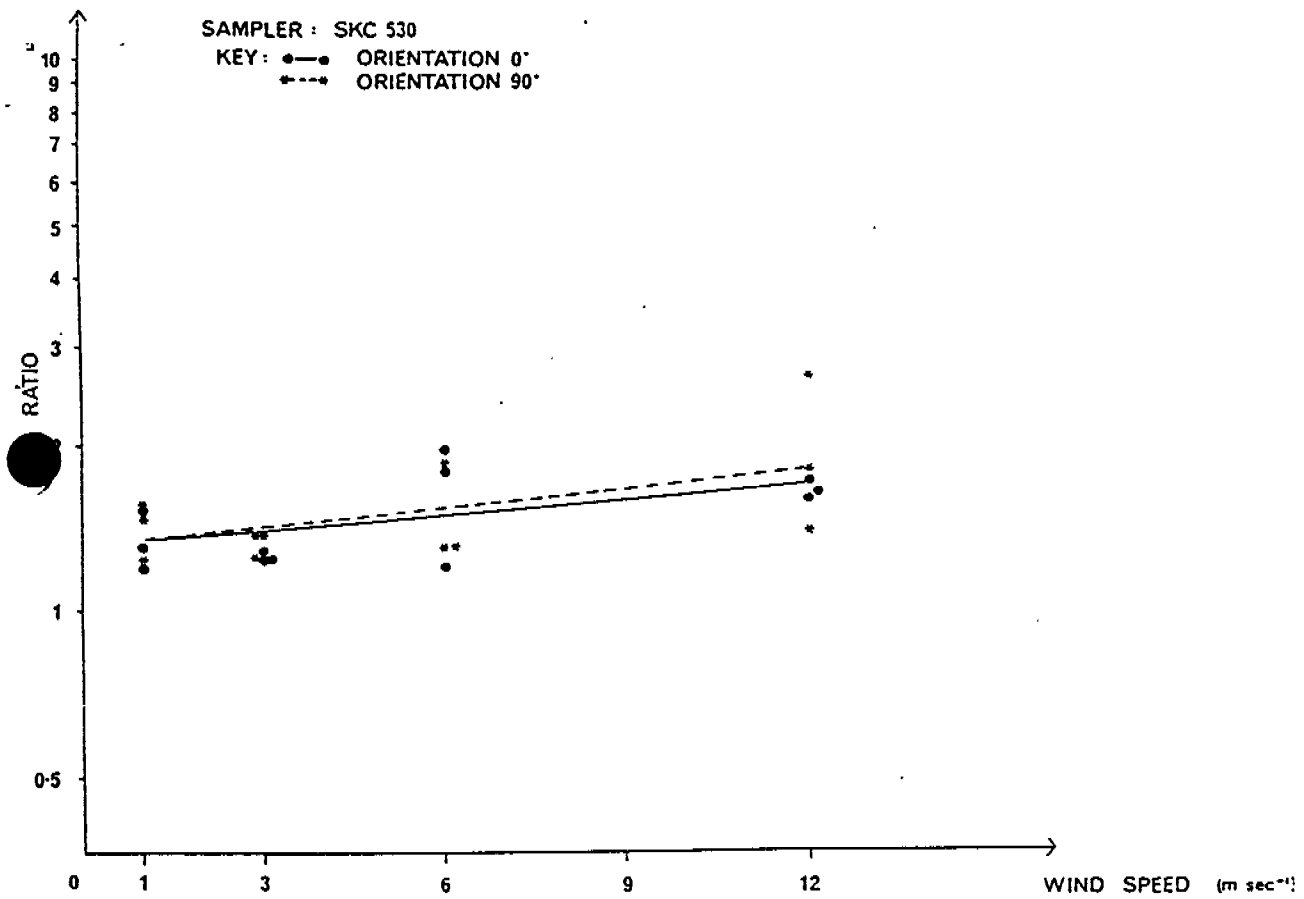


Figure 5.1 Windspeed–orientation results for SKC 530

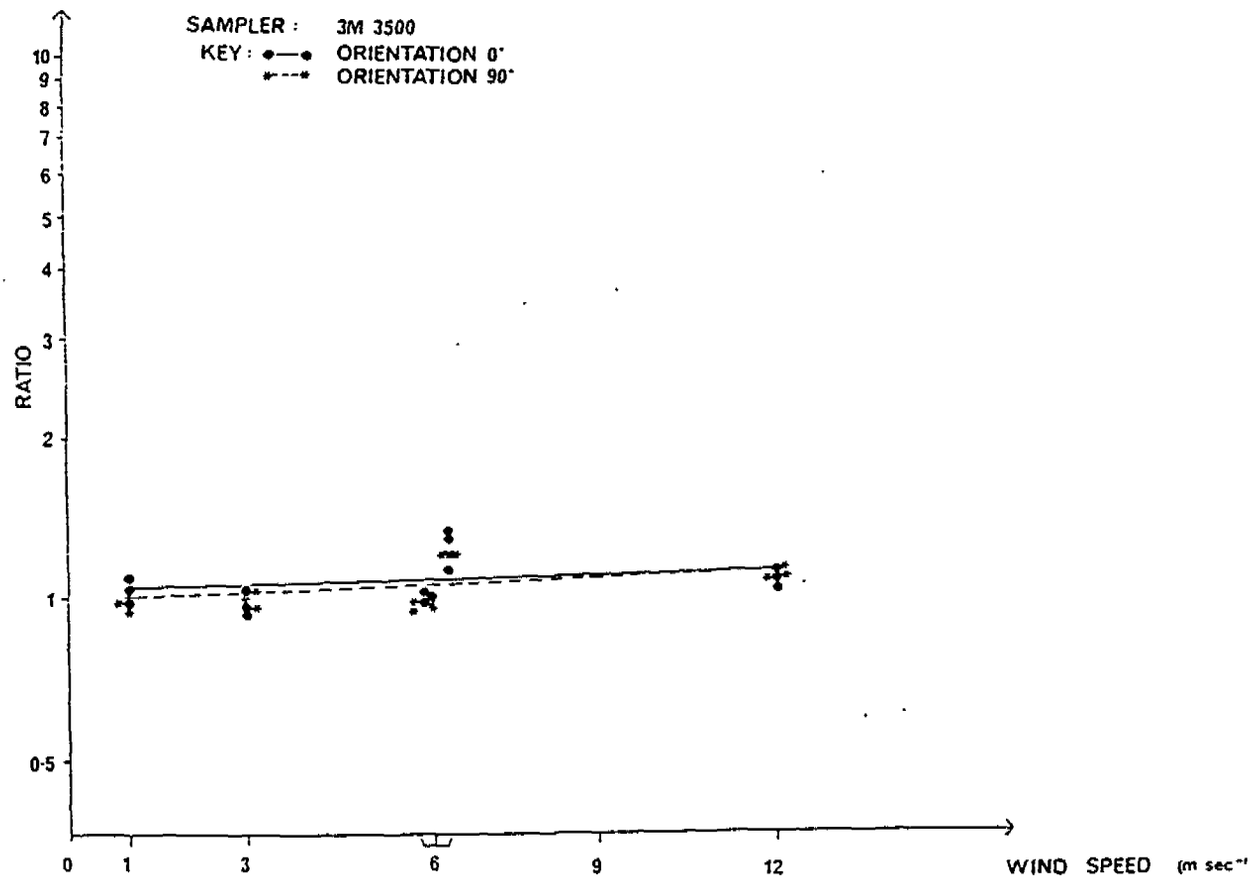


Figure 5.2 Windspeed–orientation results for 3M 3500

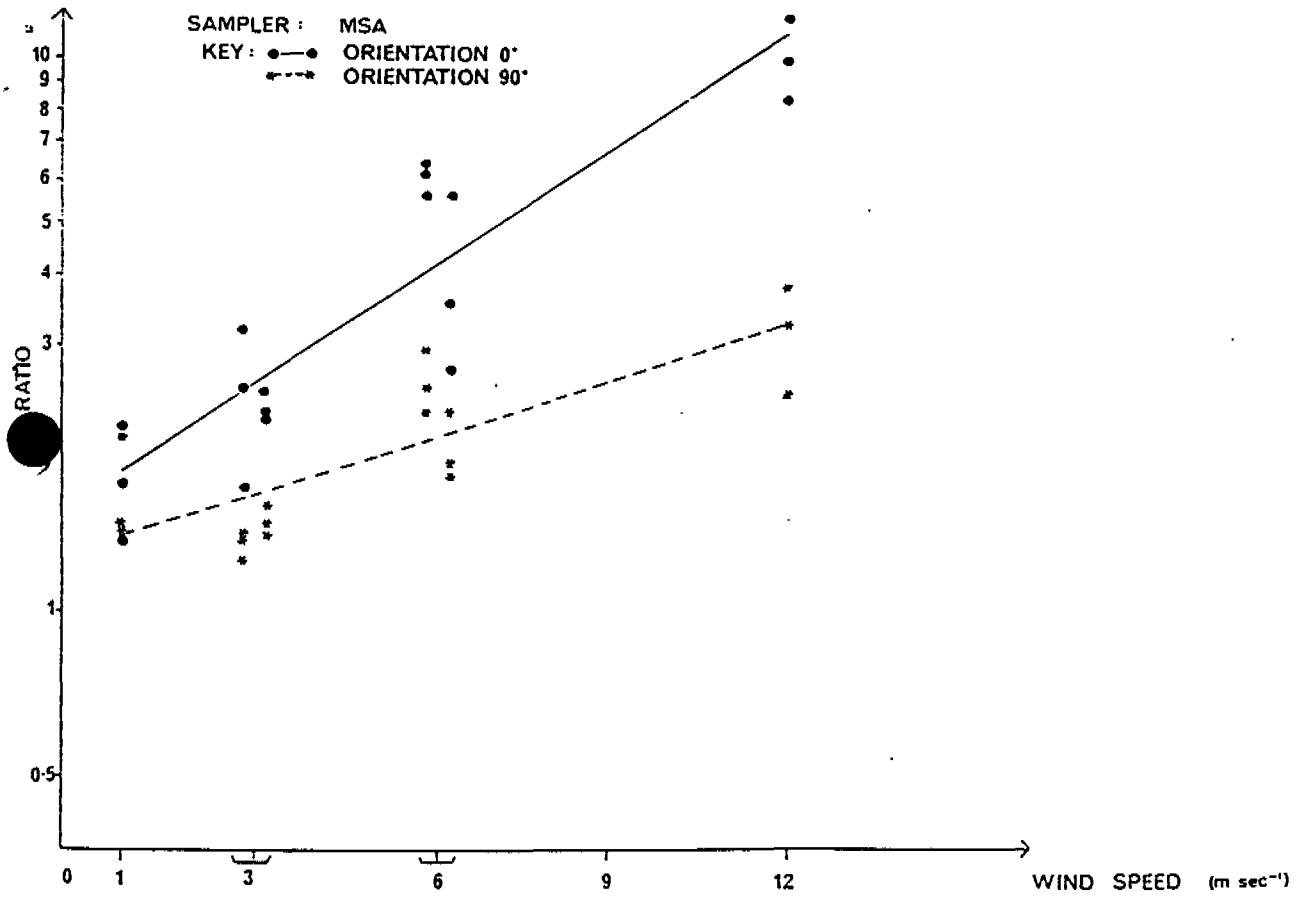


Figure 5.3 Windspeed-orientation results for MSA OVD

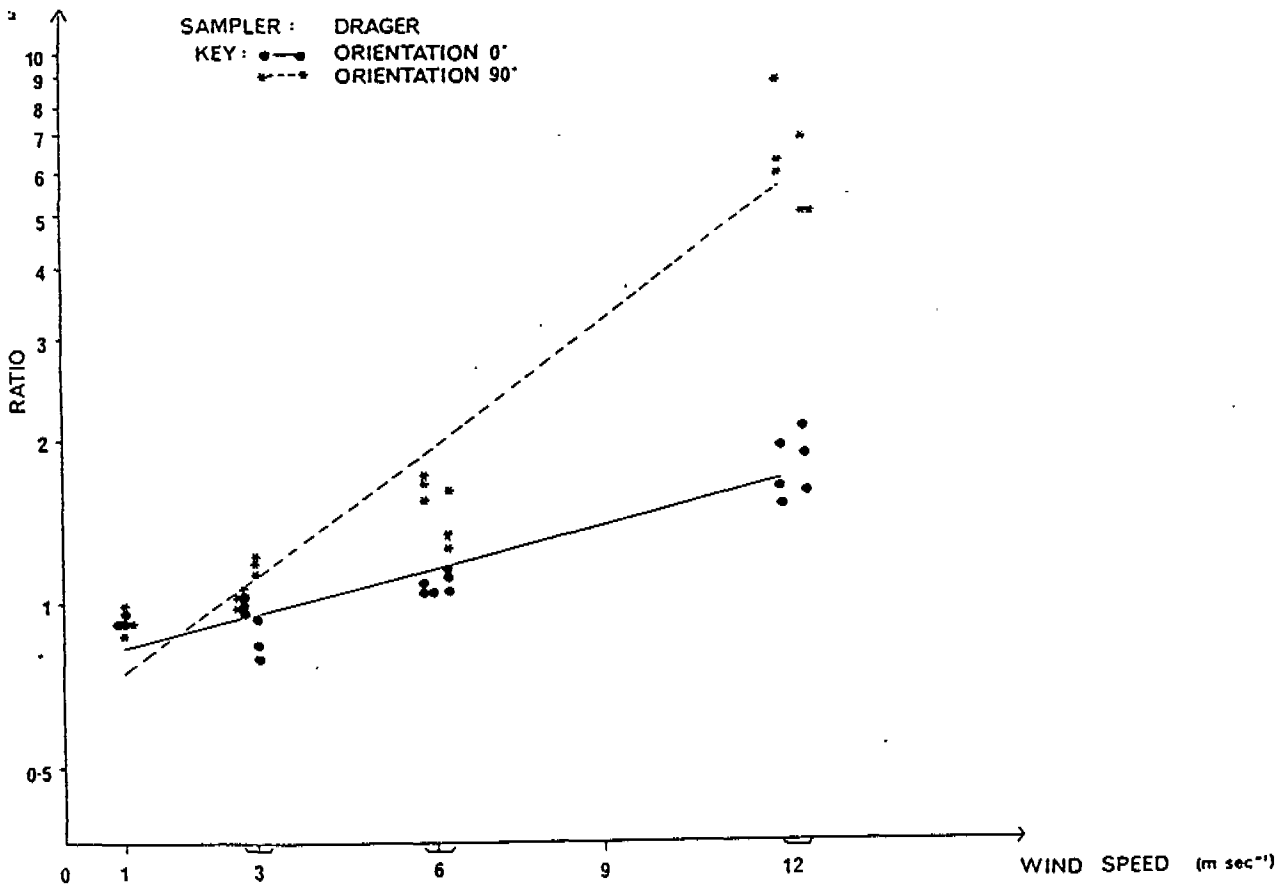


Figure 5.4 Windspeed-orientation results for Drager ORSA5

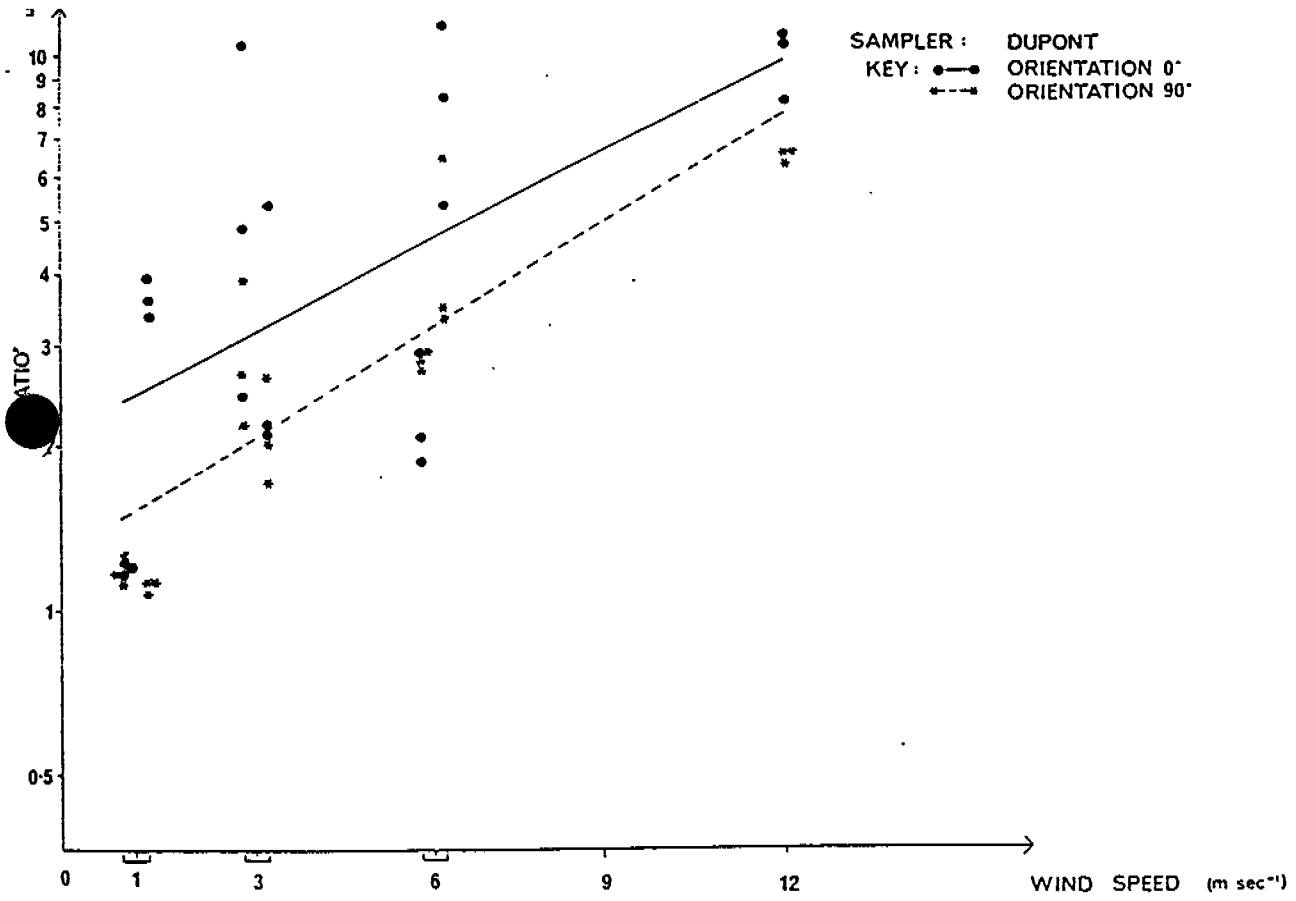


Figure 5.5 Windspeed–orientation results for Dupont PROTEC G–BB

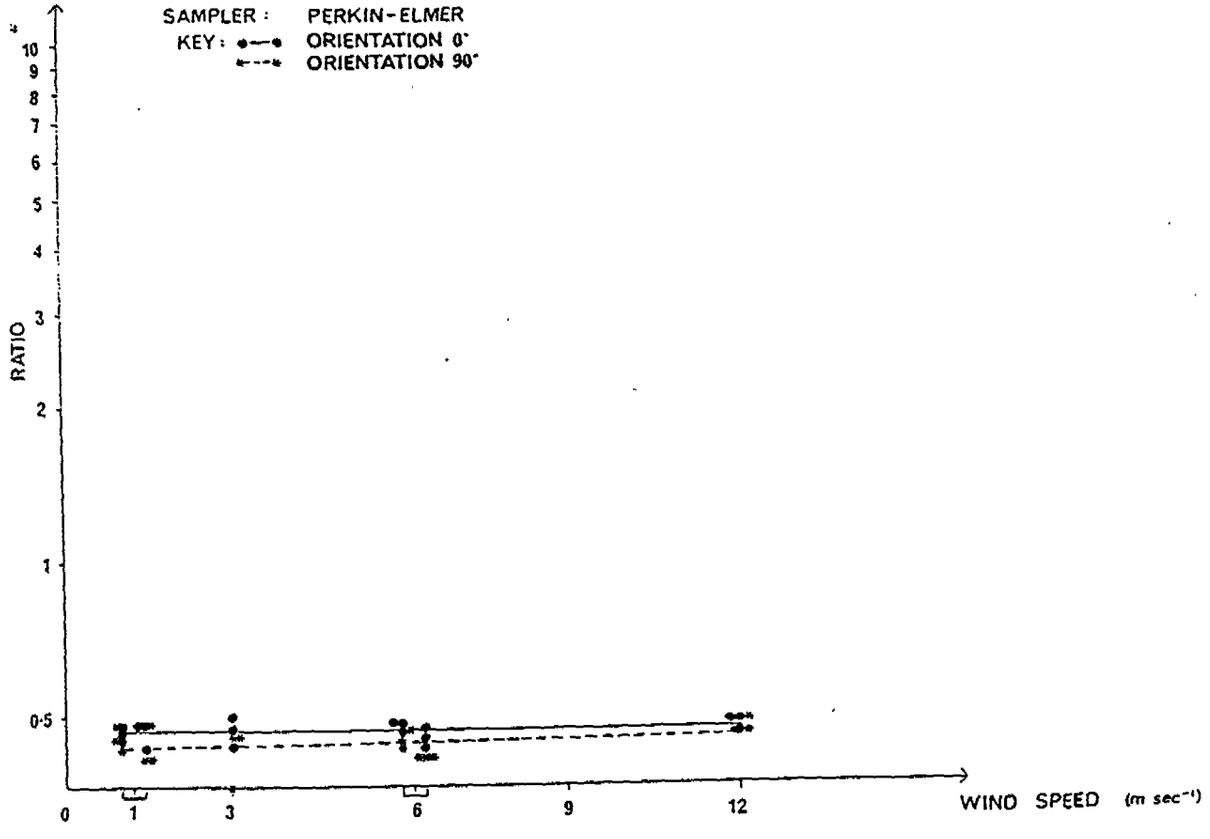


Figure 5.6 Windpeed–orientation results for Perkin Elmer ATD50

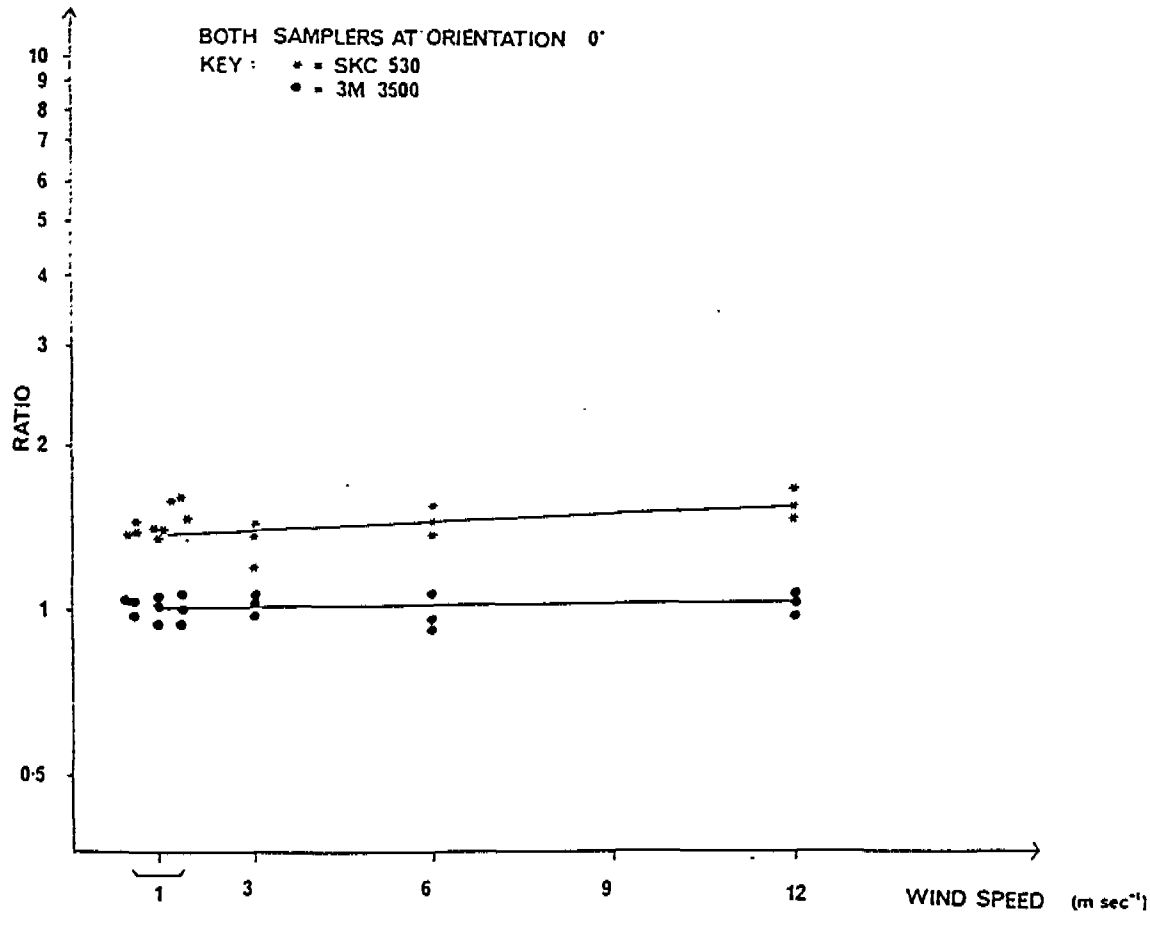


Figure 5.7 Windspeed results for SKC 530 and 3M 3500 exposed together – orientation 0°

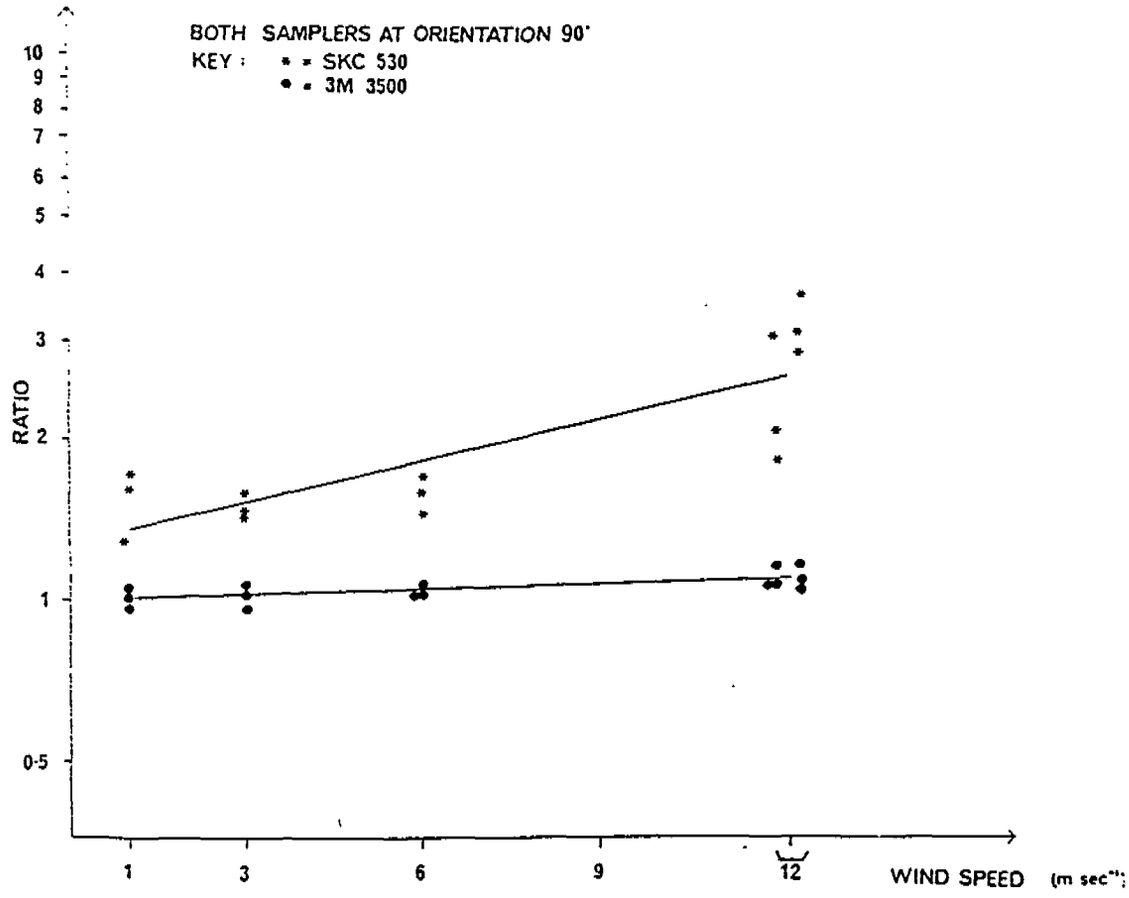


Figure 5.8 Windspeed results for SKC 530 and 3M 3500 exposed together – orientation 90°

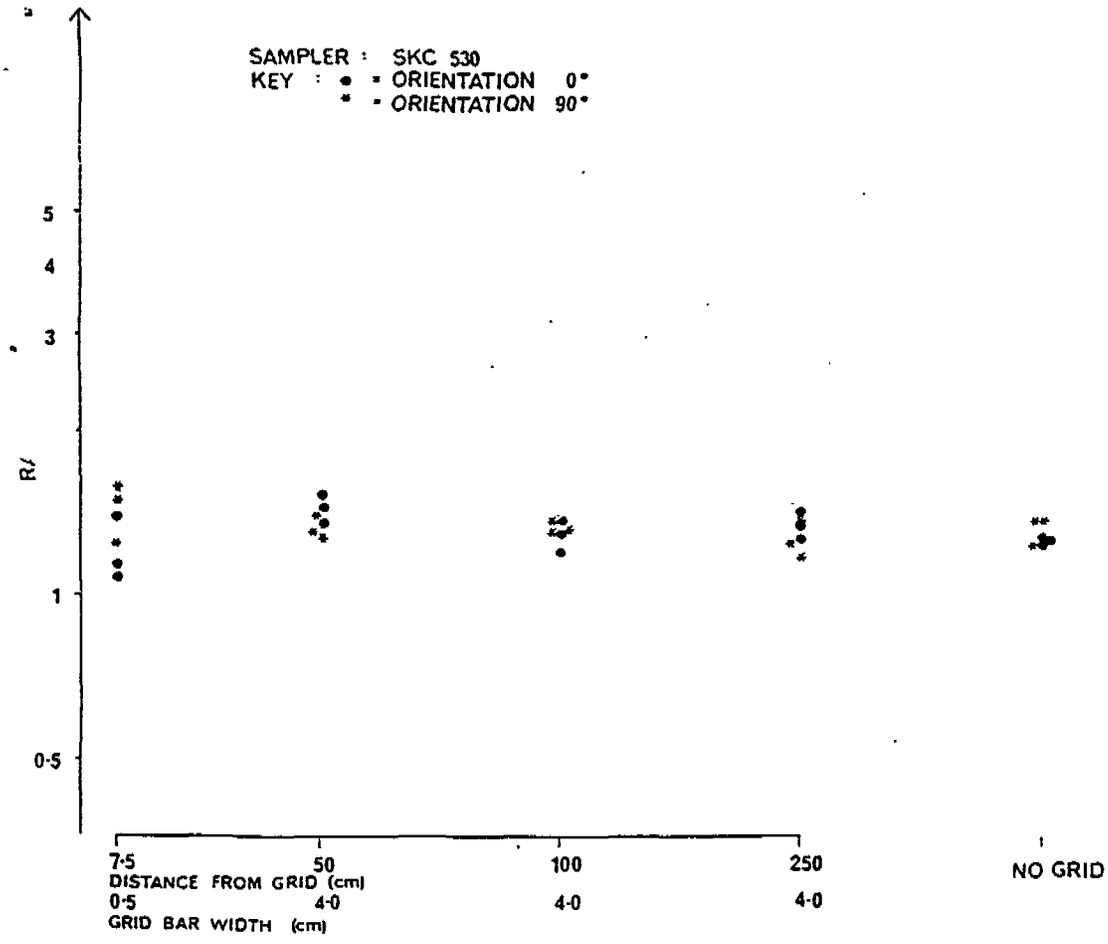


Figure 5.9 Turbulence results – SKC 530

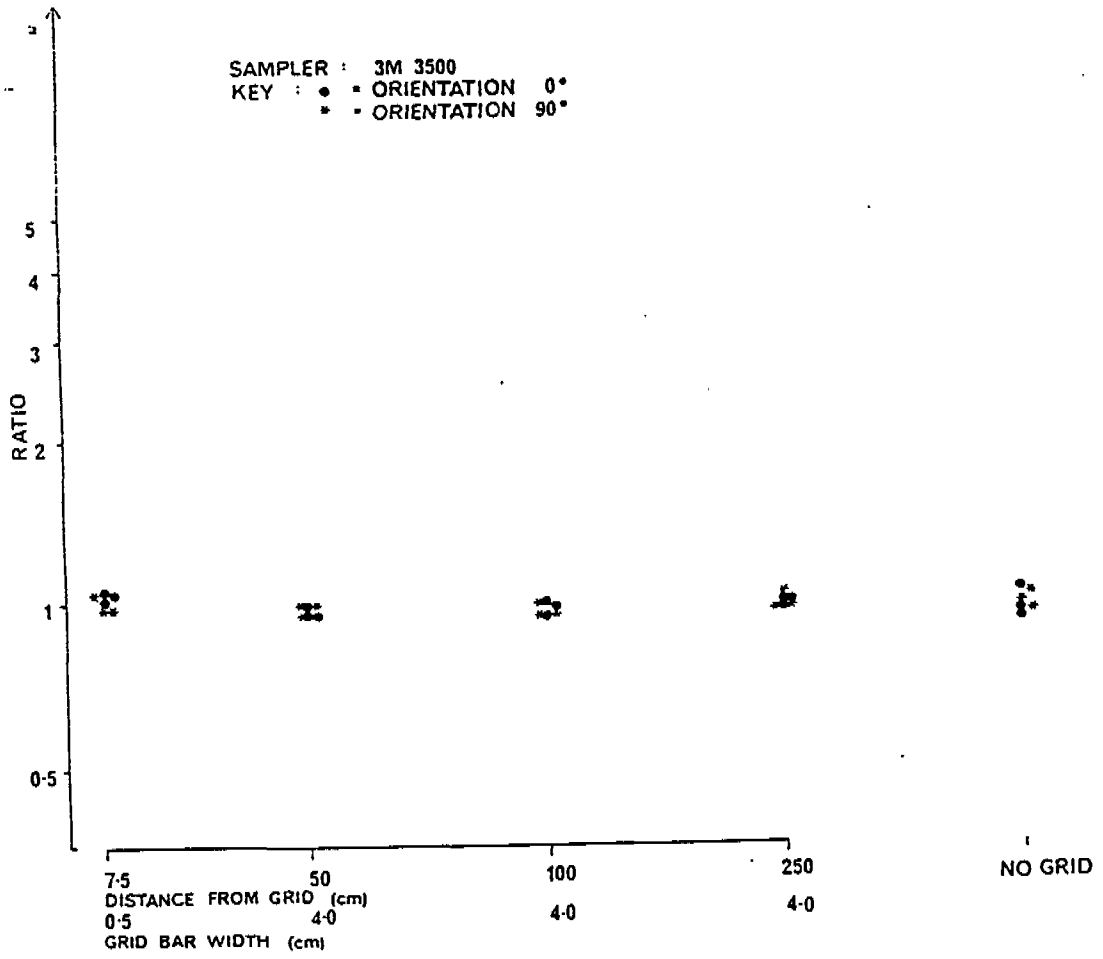


Figure 5.10 Turbulence results – 3M 3500

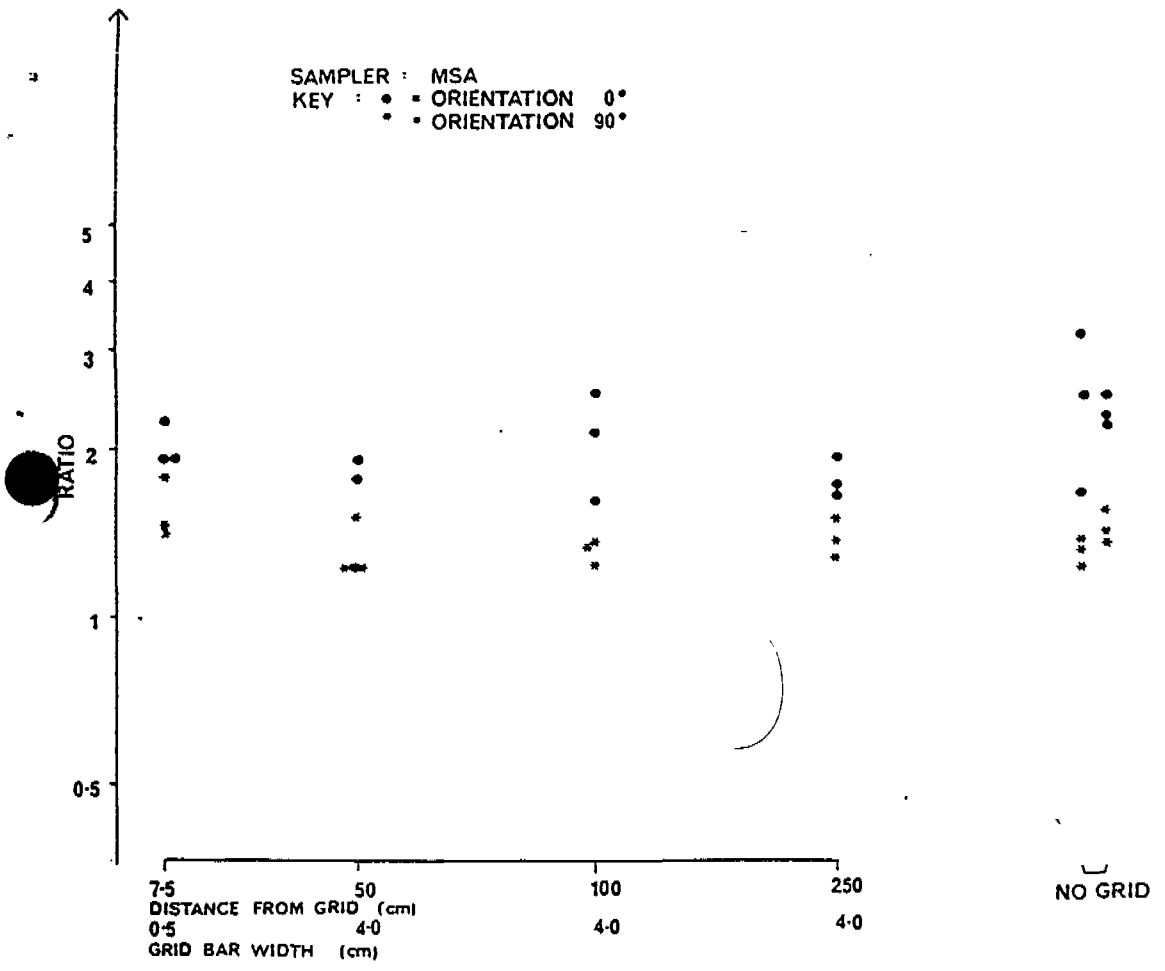


Figure 5.11 Turbulence results – MSA OVD

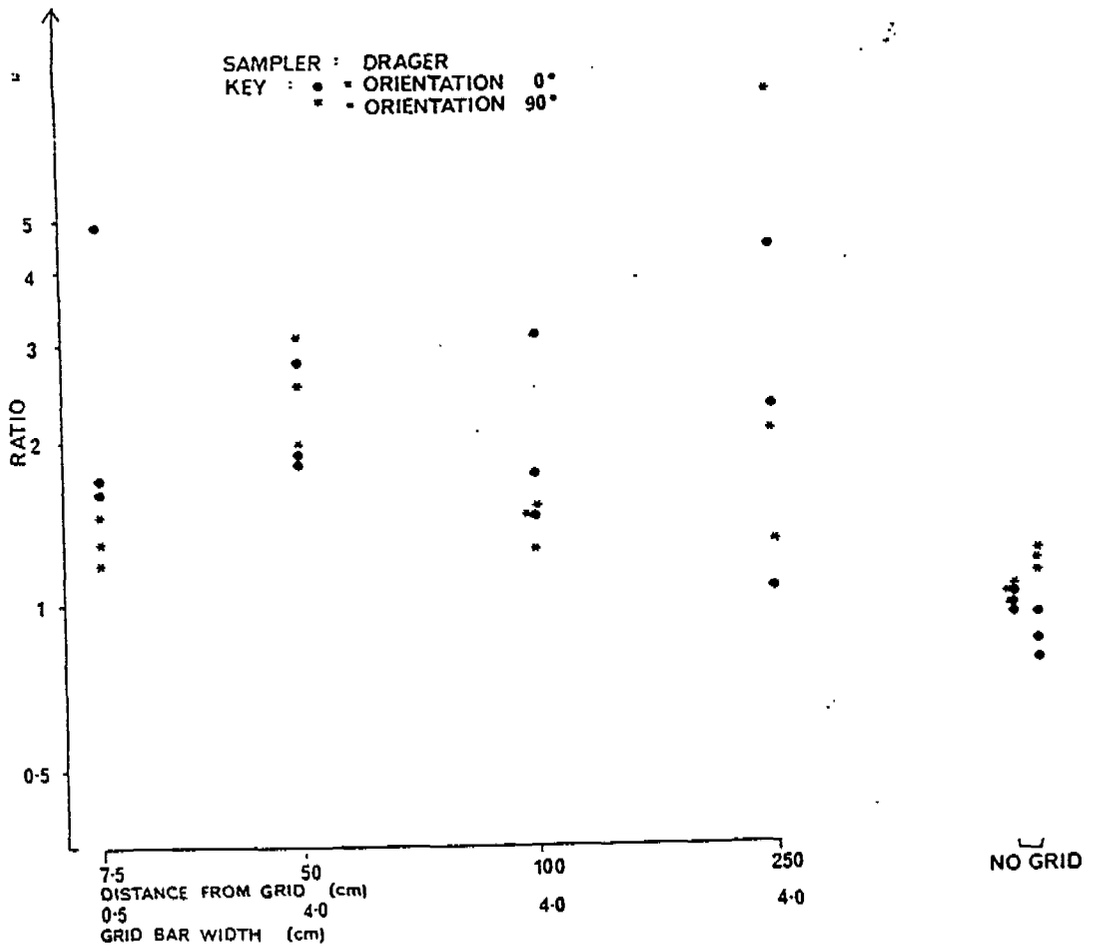


Figure 5.12 Turbulence results – Drager ORSAS

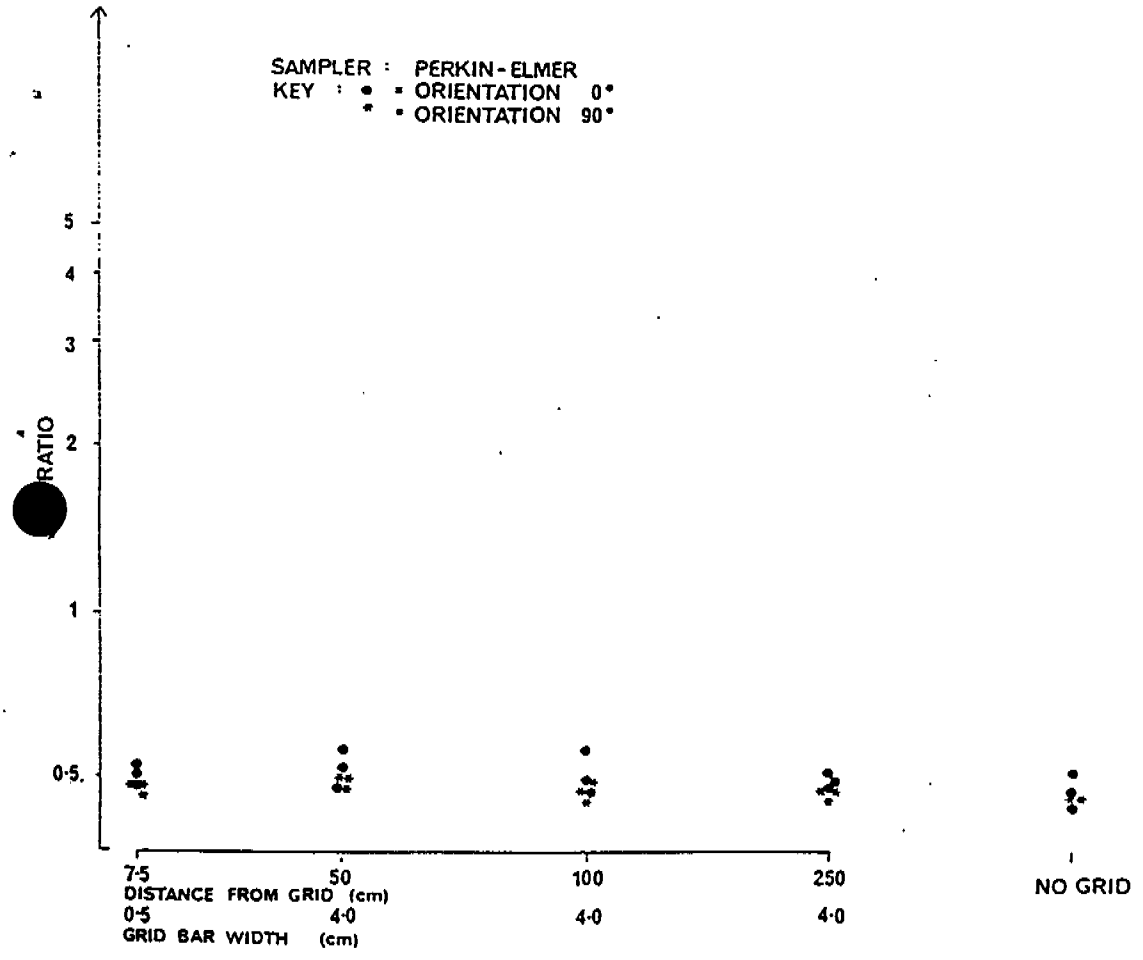


Figure 5.13 Turbulence results - Perkin Elmer ATD50

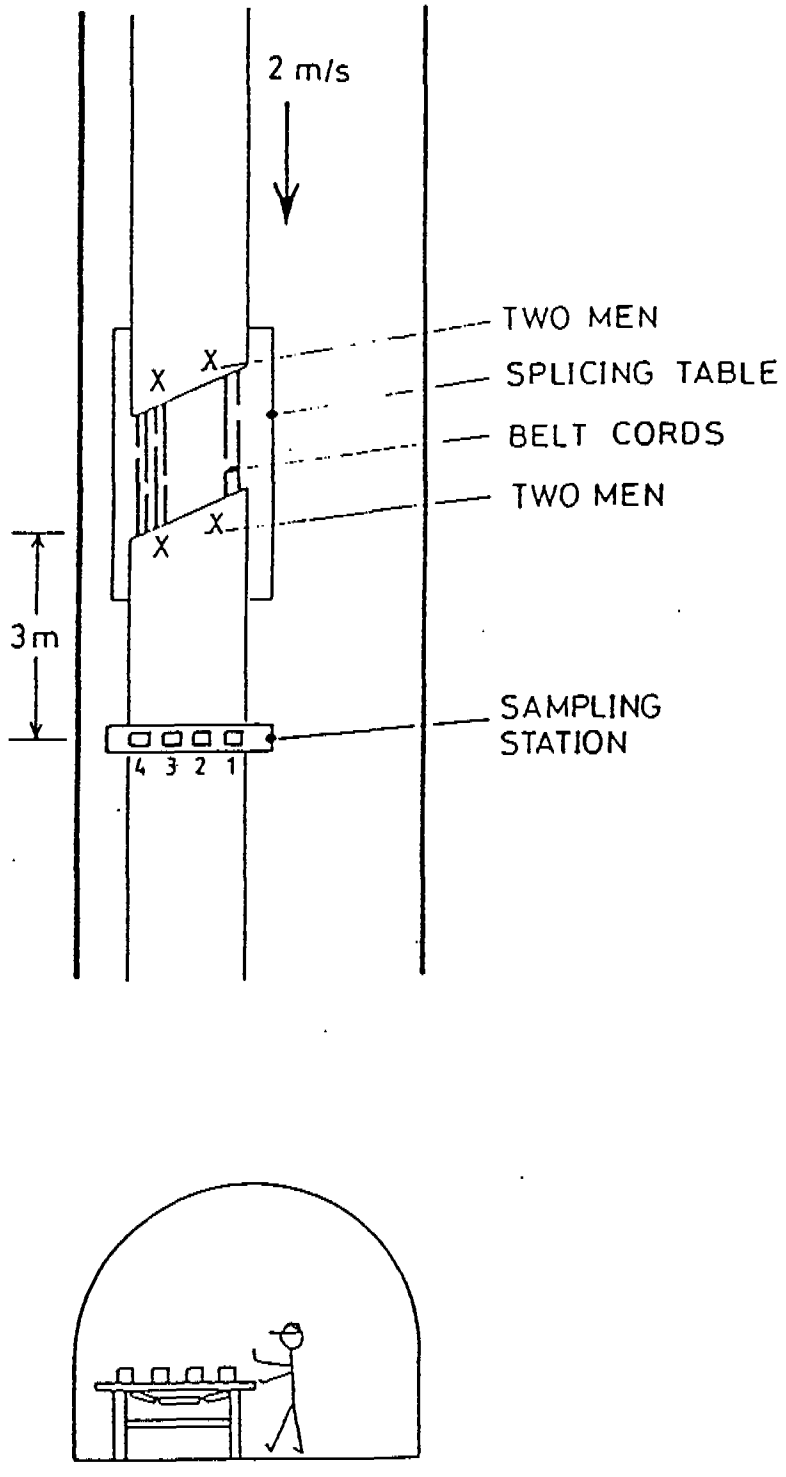


Figure 6.1 Schematic plan of test site for underground trials

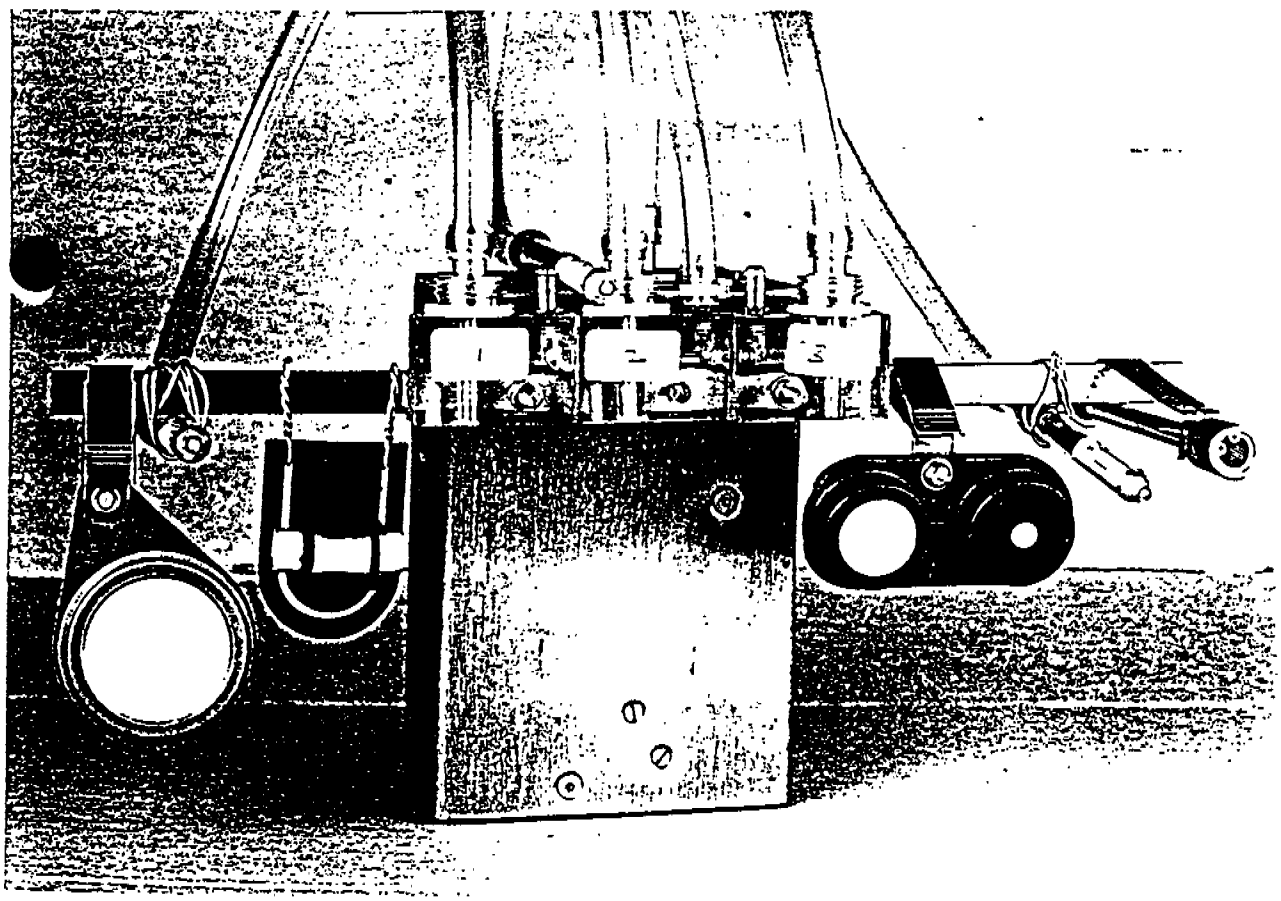


Figure 6.2 Photograph of sampling station for underground trials

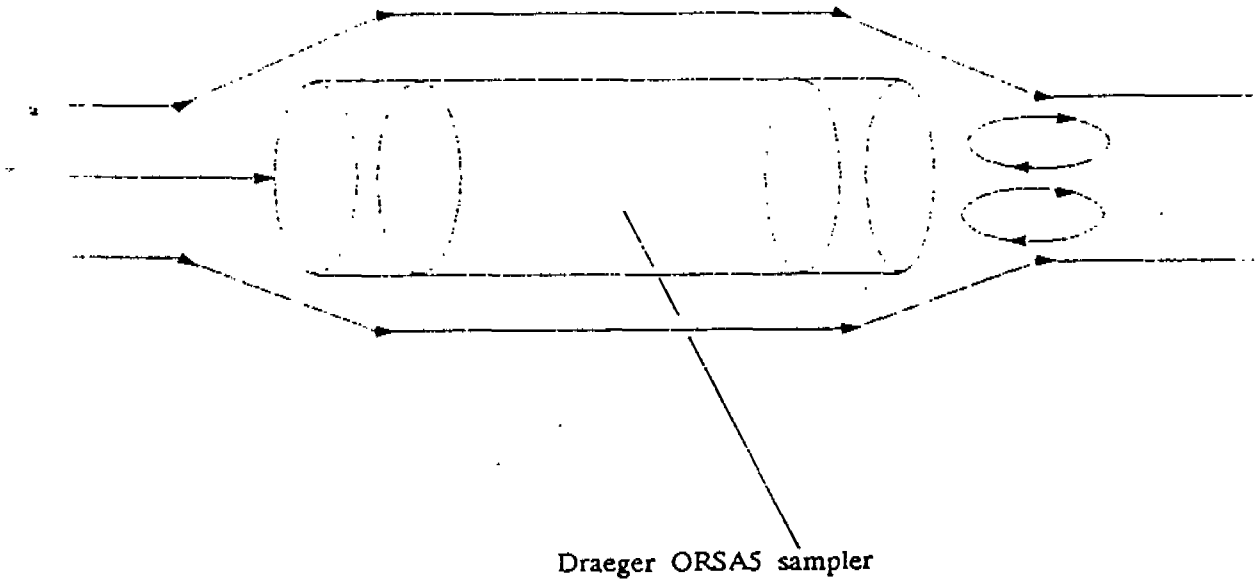


Figure 7.1 Proposed airflow pattern over Drager ORSA5 when at orientation 90°

Table 5.1 Effects of windspeed and orientation – Geometric mean of three ratios (diffusive ÷ pump) of measured vapour concentration, with geometric standard deviation in brackets, by type of sampler, windspeed and orientation. Results from runs repeated under unchanged conditions are shown on successive lines.

Type of Diffusive Sampler	Windspeed (m/s)							
	1		3		6		12	
	Orientation							
	0°	90°	0°	90°	0°	90°	0°	90°
SKC 530	1.34 (1.13)	1.41 (1.13)	1.26 (1.01)	1.32 (1.06)	1.61 (1.29)	1.46 (1.22)	1.63 (1.04)	1.87 (1.39)
3M 3500	1.04 (1.06)	0.99 (1.04)	1.01 (1.08)	0.99 (1.05)	1.26 (1.08) 1.00 (1.02)	1.21 (1.00) 0.97 (1.01)	1.09 (1.03)	1.10 (1.01)
MSA OVD	1.69 (1.26)	1.60 (1.25)	2.42 (1.40) 2.31 (1.06)	1.34 (1.06) 1.46 (1.07)	6.12 (1.06) 3.76 (1.45)	2.55 (1.15) 1.94 (1.14)	9.85 (1.20)	3.13 (1.26)
Drager	0.93 (1.02)	0.92 (1.06)	0.98 (1.04) 0.85 (1.10)	1.03 (1.03) 1.19 (1.04)	1.06 (1.01) 1.12 (1.05)	1.65 (1.05) 1.40 (1.13)	1.67 (1.14) 1.83 (1.15)	6.92 (1.25) 5.58 (1.20)
Dupont	1.20 (1.02) 3.67 (1.08)	1.18 (1.06) 1.13 (1.03)	4.99 (2.06) 2.91 (1.70)	2.86 (1.34) 2.11 (1.24)	2.24 (1.26) 7.97 (1.48)	2.82 (1.04) 4.26 (1.43)	9.73 (1.15)	6.51 (1.03)
Perkin Elmer	0.47 (1.04) 0.47 (1.07)	0.46 (1.05) 0.44 (1.11)	0.47 (1.06)	0.41 (1.18)	0.48 (1.02) 0.46 (1.04)	0.46 (1.04) 0.42 (1.04)	0.47 (1.04)	0.46 (1.04)

Table 5.2 Windspeed–orientation data (two orientations examined in each of 35 runs). Average within–run variability, expressed as the variance of the logarithm of the ratio, diffusive ÷ pump, and the geometric standard deviation of the log ratio (GSD), by sampler type, with the weighting factor used in analyses of variance.

Type of Diffusive Sampler	Variance	GSD	Weight
SKC 530	0.03105	1.193	3
3M 3500	0.00209	1.047	45
MSA OVD	0.04122	1.225	2
Drager	0.01119	1.112	8
Dupont	0.09335	1.357	1
Perkin Elmer	0.00504	1.074	18

Table 5.3 Windspeed–orientation data (two orientations examined in each of 35 runs). Weighted analysis of variance of derived variable S*.

Source of Variation	df	MS	P value
Type of diffusive sampler (T)	5	19.384	P<0.001
+ Windspeed (W)	1	5.400	P<0.001
+ W x T	5	2.630	0.05<P<0.01
Residual	23	0.129	
Total	34	3.484	

* This variable is discussed in Section 4.1 of the Report. It is defined as follows:

S = one half of the mean of three log ratios (diffusive result ÷ pump result) at orientation 0°, plus one half of the mean of three log ratios (diffusive result ÷ pump result) at orientation 90°.

Table 5.4 Windspeed–orientation data (two orientations examined in each of 35 runs). Weighted analysis of variance of derived variable D*.

Source of Variation	df	MS	P value
Orientation (O)	1	0.022	P>0.1
+ Type of diffusive sampler (T) x O	5	1.056	P<0.001
+ Windspeed (W) x O	1	0.580	P<0.001
+ W x T x O	5	0.593	P<0.001
Residual	23	0.036	
Total	35	0.275	

* This variable is discussed in Section 4.1 of the Report. It is defined as follows:

D = one half of the mean of three log ratios (diffusive result ÷ pump result) at orientation 0°, minus one half of the mean of three log ratios (diffusive result ÷ pump result) at orientation 90°.

Table 5.5 Windspeed–orientation data (two orientations examined in each of 35 runs). Estimated slopes and intercepts (estimated standard errors in brackets) of regression lines relating windspeed to the derived variables S and D†.

Type of Diffusive Sampler	(i) – S		(ii) – D	
	Intercept	Slope	Intercept	Slope
SKC 530	0.250 (0.172)	0.0255 (0.0250)	0.0011 (0.0879)	-0.0035 (0.0128)
3M 3500	0.013 (0.043)	0.0087 (0.0064)	0.0273 (0.0221)	-0.0024 (0.0033)
MSA OVD	0.341 (0.184)	0.1204 (0.0294)***	0.0881 (0.0939)	0.0442 (0.0150)**
Drager	-0.363 (0.087)***	0.1245 (0.0119)***	0.1077 (0.0446)*	-0.0592 (0.0061)***
Dupont	0.485 (0.220)*	0.1402 (0.0380)**	0.2581 (0.1125)*	-0.0116 (0.0194)
Perkin Elmer	-0.796 (0.056)***	0.0022 (0.0091)	0.0363 (0.0286)	-0.0013 (0.0046)

† See footnotes to Tables 5.3 and 5.4.

* P<0.05; ** P<0.01; ***P<0.001.

Table 5.6 Windspeed–orientation data (two orientations examined in each of 35 runs). Estimated slopes and intercepts (estimated standard errors in brackets) of regression lines relating windspeed to the mean of three log ratios (diffusive result ÷ pump result), by orientation and sampler type.

Type of Diffusive Sampler	Parameter					
	Intercept		(e.s.e.)	Slope		(e.s.e.)
	Orientation 0°	90°		Orientation 0°	90°	
SKC	0.251	0.249	(0.193)	0.0220	0.0290	(0.0281)
3M	0.040	-0.014	(0.048)	0.0063	0.0111	(0.0072)
MSA	0.429*	0.253	(0.207)	0.1646***	0.0762*	(0.0330)
Drager	-0.255*	-0.471***	(0.098)	0.0653***	0.1837***	(0.0134)
Dupont	0.743**	0.227	(0.247)	0.1286**	0.1518**	(0.0427)
Perkin Elmer	-0.760***	-0.832***	(0.063)	0.0009	0.0035	(0.0102)

* $P<0.05$; ** $P<0.01$; *** $P<0.001$.

Table 5.7 Effects of windspeed and orientation runs (SKC 530 and 3M 3500 only, used together in each of 11 runs). Geometric mean of three ratios (diffusive ÷ pump) of measured vapour orientation, with geometric standard deviation in brackets, by type of sampler, windspeed and orientation. Results from runs repeated under unchanged conditions are shown on successive lines.

Orientation	Windspeed (m/s)							
	1		3		6		12	
	Type of diffusive sampler							
	SKC 530	3M 3500	SKC 530	3M 3500	SKC 530	3M 3500	SKC 530	3M 3500
0°	1.40 (1.03)	1.01 (1.04)	1.33 (1.09)	1.01 (1.04)	1.45 (1.06)	0.99 (1.08)	1.56 (1.06)	1.03 (1.03)
	1.37 (1.01)	0.98 (1.04)						
	1.56 (1.04)	1.00 (1.06)						
90°	1.51 (1.15)	1.01 (1.04)	1.50 (1.05)	1.05 (1.03)	1.57 (1.10)	1.03 (1.01)	2.25 (1.34)	1.10 (1.05)
							3.19 (1.14)	1.11 (1.05)

Table 5.8 Windspeed–orientation data – SKC device. Analysis of variance of the within–run mean of three log ratios (diffusive result ÷ pump result).

Source of Variation	df	MS	P value
Windspeed (W)	1	0.355	0.001<P<0.005
+ Orientation (O)	1	0.087	0.05<P<0.1
+ W x O	1	0.127	0.025<P<0.05
Residual	7	0.016	
Total	10	0.068	

Table 5.9 Windspeed–orientation data – 3M 3500 device. Analysis of variance of the within–run mean of three log ratios (diffusive result ÷ pump result).

Source of Variation	df	MS	P value
Windspeed (W)	1	0.00881	P<0.001
+ Orientation (O)	1	0.00435	0.005<P<0.01
+ W x O	1	0.00151	0.005<P<0.1
Residual	7	0.00028	
Total	10	0.00166	

Table 5.10 Windspeed–orientation data (SKC 530 and 3M 3500 only, used together in each of 11 runs).
Estimated slopes and intercepts (estimated standard errors in brackets) of regression lines relating windspeed to the mean of three log ratios (diffusive result ÷ pump result), by orientation and sampler type.

Diffusive Sampler	Orientation			
	0°		90°	
	Intercept	Slope	Intercept	Slope
SKC	0.3352 (0.0739)**	0.0075 (0.0131)	0.2522 (0.1032)*	0.0580 (0.0126)**
3M	-0.0064 (0.0097)	0.0020 (0.0017)	0.0061 (0.0135)	0.0075 (0.0024)*

* $P<0.05$; ** $P<0.01$.

Table 5.11 Effects of Turbulence - Geometric mean of three ratios (diffusive ÷ pump) of measured vapour concentration, with geometric standard deviation in brackets, by type of sampler, turbulence condition, and orientation. Results from runs repeated under unchanged conditions are shown on successive lines.

Type of Diffusive Sampler	Distance (cm)								No grid. (Data from windspeed/orientation runs - windspeed = 3 m/s)	
	7.5		60		100		250			
	Grid bar width (cm)									
	0.5		4.0		4.0		4.0			
	Orientation								Orientation	
	0°	90°	0°	90°	0°	90°	0°	90°	0°	90°
SKC	1.20 (1.13)	1.14 (1.13)	1.44 (1.05)	1.34 (1.05)	1.28 (1.06)	1.34 (1.02)	1.34 (1.07)	1.27 (1.06)	1.26 (1.01)	1.32 (1.06)
3M	1.01 (1.03)	1.00 (1.05)	0.98 (1.04)	0.98 (1.03)	0.98 (1.02)	0.97 (1.02)	0.99 (1.01)	0.98 (1.03)	1.01 (1.08)	0.99 (1.05)
MSA	2.01 (1.09)	1.56 (1.14)	1.61 (1.27)	1.32 (1.12)	2.08 (1.25)	1.34 (1.05)	1.78 (1.09)	1.40 (1.07)	2.12 (1.40) 2.31 (1.06)	1.34 (1.06) 1.46 (1.07)
Drager	2.38 (1.86)	1.32 (1.09)	2.12 (1.26)	2.49 (1.25)	1.99 (1.49)	1.41 (1.10)	2.22 (2.01)	2.83 (2.66)	0.98 (1.04) 0.85 (1.10)	1.03 (1.03) 1.19 (1.04)
Perkin Elmer	0.50 (1.03)	0.49 (1.06)	0.52 (1.08)	0.49 (1.03)	0.51 (1.08)	0.47 (1.04)	0.49 (1.05)	0.46 (1.02)	0.17 (1.06)	0.41 (1.18)

Table 5.12 Turbulence data.
Weighted analysis of variance of derived variable S⊗.

Source of variation	df	MS	Variance ratio*	P value†
Type of diffusive sampler (T)	4	28.8157	116.47	P<0.001
+ Turbulence condition (0)	4	0.0473	0.19	P>0.1
+ T x 0	16	0.0950	0.38	P>0.1
Residual	2	0.0008		
Total	26	4.4990		

⊗ See footnote to Table 5.3.
* Obtained by dividing the MS column by 0.2474.
† Degrees of freedom of residual = 23.

Table 5.13 Turbulence data.
Weighted analysis of variance of derived variable D⊗.

Source of variation	df	MS	Variance ratio*	P value†
Orientation (0)	1	0.2319	3.60	0.05<P<0.1
+ Type of diffusive sampler (T) x 0	4	0.3563	5.53	0.001<P<0.005
+ Turbulence condition (C) x 0	4	0.0150	0.23	P>0.1
+ T x C x 0	16	0.0475	0.74	P>0.1
Residual	2	0.0129		
Total	27	3.1111		

⊗ See footnote to Table 5.4.
* Obtained by dividing the MS column by 0.0644.
† Degrees of freedom of residual = 23.

Table 5.14 Effects of vapour concentration, loading and sampling time.
Geometric means of three ratios (diffusive ÷ pump) of measured vapour concentration, with geometric standard deviations in brackets, by experimental conditions and sampler type.
Results from repeat runs under unchanged conditions appear on successive lines.

Vapour Concentration (mg/m^3)	Time (min)	Diffusive sampler					
		SKC	3M	MSA	Drager	Perkin Elmer	
		Orientation					
		0°	0°	0°	0°	0°	90°
5	180	2.87 (1.10)	1.03 (1.08)				
40	60	1.33 (1.09)*	1.01 (1.08)*	2.42 (1.40)	0.98 (1.04)*	0.47 (1.06)*	0.41 (1.18)*
			1.01 (1.04)*	2.31 (1.06)	0.85 (1.10)*		
	80	1.35 (1.17)	0.96 (1.13)				
	90	1.26 (1.01)*					
	180			2.12 (1.14)*	0.88 (1.07)	0.47 (1.02)	0.44 (1.04)
	360	1.26 (1.08)	0.94 (1.04)	2.13 (1.26)*	0.90 (1.05)	0.45 (1.01)	0.44 (1.05)
			0.93 (1.02)				
100	60	1.40 (1.09)	0.94 (1.05)	1.69 (1.13)	0.93 (1.05)	0.52 (1.03)	0.50 (1.02)
200	60	1.34 (1.06)	0.98 (1.06)	2.14 (1.14)	0.93 (1.10)	0.49 (1.03)	0.47 (1.05)

* Data from windspeed-orientation runs.

Table 5.15(a) Concentration-time data.
Analyses of variance of the mean of three log ratios (diffusive result ÷ pump result), for four samplers.

Diffusive Sampler	Source of Variation	*df*	MS	VR*	P value
SKC	Experimental Conditions	4	0.1300	8.84	P<0.001
	Residual	2	0.0012		
	Total	6	0.0871		
3M	Experimental Conditions	4	0.0022	0.27	P>0.1
	Residual	3	0.0005		
	Total	7	0.0015		
MSA	Experimental Conditions	4	0.0189	0.29	P>0.1
	Residual	1	0.0011		
	Total	5	0.0153		
Drager	Experimental Conditions	4	0.0004	0.05	P>0.1
	Residual	1	0.0102		
	Total	5	0.0024		

* The residual mean squares used to obtain the variance ratios in the above Tables are, respectively: 0.0147, 0.0081, 0.0644 and 0.0085, assumed to have 14, 16, 12 and 12 degrees of freedom.

Table 5.15(b) Concentration-time data - Perkin Elmer device.

(i) Analysis of variance of derived variable S**.

Source of variation	df	MS	Variance ratio†	P value
Experimental Conditions	4	0.0038	0.65	P>0.25

† The residual mean square used to obtain the variance ratio is 0.0058, with 20 degrees of freedom.

** See footnote to Table 5.3.

(ii) Analysis of variance of derived variable D††.

Source of variation	df	MS	Variance ratio⊗	P value
Orientation (O)	1	0.004351	2.88	0.1<P<0.25
Experimental conditions x O	4	0.000510	0.34	P>0.25
Total	5	0.001278		

⊗ The residual mean square used to obtain the variance ratio is 0.0015, with 20 degrees of freedom.

†† See footnote to Table 5.4.

Table 5.16 Effects of fluctuating vapour concentrations.
Geometric means of three ratios (diffusive ÷ pump) of measured vapour concentration, with geometric standard deviations in brackets, by experimental condition and sampler type. Results from runs repeated under unchanged conditions are shown on successive lines (Drager device only).

Diffusive Sampler	Run time (min)				Steady Concentration (Data from windspeed-orientation runs; windspeed = 3m sec^{-1})	
	10		480			
	Orientation		Orientation		Orientation	
	0°	90°	0°	90°	0°	90°
SKC 530	1.45 (1.02)		1.44 (1.01)		1.26 (1.01)	
3M 3500	1.00 (1.02)		0.96 (1.00)		1.01 (1.08)	
Drager		1.12 (1.04)		1.11 (1.02)		1.03 (1.03)
						1.19 (1.04)
Perkin Elmer		0.48 (1.05)		0.38 (1.05)		0.41 (1.18)

Table 5.17 Effects of Dust Exposure.
Geometric means of three ratios* (diffusive ÷ pump) of measured vapour concentration, with geometric standard deviations in brackets, by experimental condition and sampler type.

Dust Type	Dust Concentration	Diffusive Sampler			
		SKC 530	3M 3500	Drager	Perkin Elmer*
Aloxite	Low	1.42 (1.03)	0.98 (1.02)	1.05 (1.00)	0.45 (1.07)
Pulverised Fuel	High	1.34 (1.00)	0.98 (1.02)	0.97 (1.00)	0.46 (1.03)

* Six results were obtained for the Perkin Elmer within each run.

Table 6.1 Uptake rates for toluene.

Sampler	Uptake rate (ml/min)*	
	Manufacturers	Experimentally determined
SKC 530	9.05	12.82
3M 3500	31.4	33.0
Drager Orsa 5	6.06	6.69
Perkin Elmer ATD 50	0.635	0.317

* Expressed as an equivalent air sampling flow rate for a pumped sampler.

Table 6.2 Field trial.
Single measurements of vapour concentrations (ppm) for diffusive samplers; means of 2, 3 or 4 measurements for pumped tubes.

Run	Sampler	Sampling Station			
		1	2	3	4
1	Pumped Tube	24.4	26.0	30.5	34.5
	Perkin Elmer	31.9	31.7	32.3	34.9
	3M 3500	28.1	29.4	29.7	32.4
	Drager	28.6	28.6	31.3	34.0
	SKC 530	28.9	31.9	33.5	37.6
2	Pumped Tube	49.8	59.4	66.1	71.2
	Perkin Elmer	60.5	62.9	76.6	81.8
	3M 3500	62.2	66.1	80.2	82.0
	Drager	52.4	67.2	65.9	70.4
	SKC 530	50.4	69.8	77.0	88.9

Table 6.3 Field Trial.
Analysis of variance of the Natural Logarithm of measured vapour concentration (ppm).

Source of variation	df	MS*	Variance ratio	P value
Sampler (S)	4	0.0276	4.00	P=0.1
Position (P)	3	0.1458		
Run (R)	1	6.0598		
S x P	12	0.0041	1.47	P=0.25
S x R	4	0.0069		
P x R	3	0.0161		
S x P x R	12	0.0028		
Total	39			

* 'F' test of S uses the MS for S x R as denominator.
'F' test of S x P uses the MS for S x P x R as denominator.

Table 7.1 Ratio of uptake rates for diffusive samplers for 1,1,1 trichloroethane and toluene.

Type of Diffusive Sampler	Ratio of Uptake Rates Experimental/Manufacturers	
	1,1,1 trichloroethane*	toluene
SKC 530	1.41	1.42
3M 3500	1.01	1.05
Drager Orsa 5	0.92	1.11
Perkin Elmer ATD 50	0.46	0.50

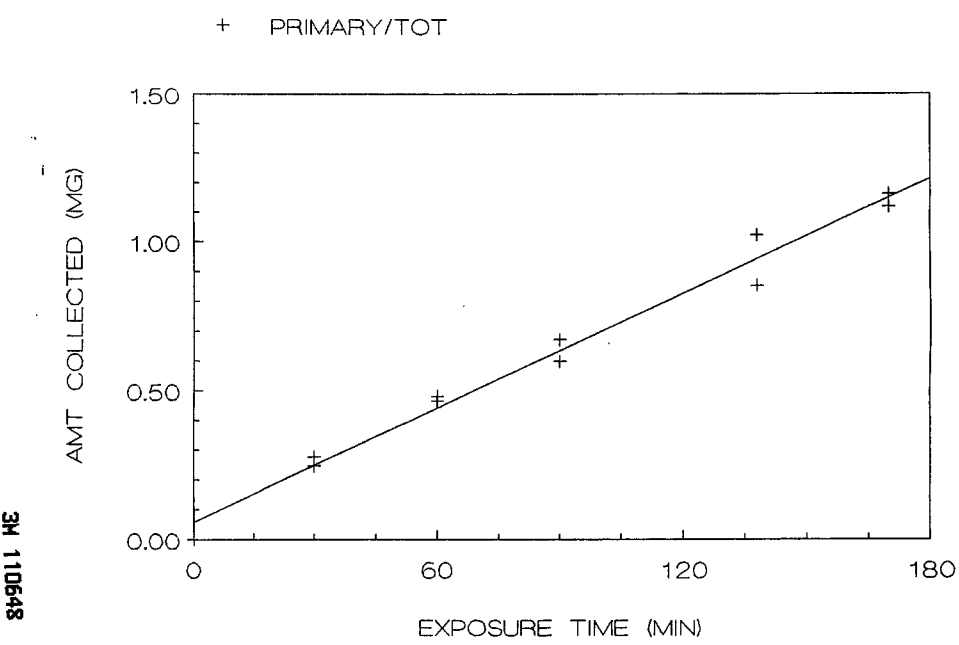
* This ratio was based on the average ratio of diffusive to pumped concentrations at 1m/sec, quoted in Section 5.

Table 8.1 Summary of conclusions from work.

Type of Diffusive Sampler	Validity of Manufacturer's Uptake Rate	Effect of Windspeed/ Orientation	Effect of Turbulent Airflows	Effect of Vapour Loading	Effect of Initial 'Spike'	Effect of Airborne Dust	Underground Trial - Toluene	Potentially Suitable for Coalmine Use
SKC 530	1,1,1 TCE gives results with bias +40%	Not statistically significant	Not statistically significant	No effect at most conc's tested	Not statistically significant	Not statistically significant	Consistent results - small bias	Yes
3M 3500	OK	Not statistically significant	Not statistically significant	Not statistically significant	Not statistically significant	Not statistically significant	Consistent results - small bias	Yes
NSA OVD	1,1,1 TCE gives results with bias +60%	Results very variable - affected by both wind & orientation	Not statistically significant	Not statistically significant	DROPPED FROM FURTHER EVALUATION			No
Drager Orsa 5	1,1,1 TCE gives results with bias -8%	Affected by both wind & orientation at high windspeeds	Introduces bias and random variation into results	Not statistically significant	Not statistically significant	Small unimportant effects	Consistent results - small bias	No
Dupont Protec G-BB	Results too variable to assess	Results very variable - affected by both wind & orientation	DROPPED FROM FURTHER EVALUATION					No
Perkin Elmer ATD 50	1,1,1 TEC gives results with bias -44%	Not statistically significant	Not statistically significant	Not statistically significant	Some loss of vapour (different adsorbent may be better)	Not statistically significant	Consistent results - small bias	Yes

3M 3520 OVM

DUPONT HCFC123 EXPOSURE • 39 PPM DRY



3M 110648

HEXACHLOROETHANE RECOVERY				
.5EL				
amt spike,ug	amt rec	rec	avg rec	std dev
62.2	52.89	0.850322		
62.2	54.97	0.883762		
62.2	50.39	0.810129		
62.2	48.74	0.783601	0.83	0.04
1EL				
amt spike,ug	amt rec	rec	avg rec	std dev
124.4	101.55	0.816318		
124.4	108.89	0.875322		
124.4	105.87	0.851045		
124.4	104.4	0.839228	0.85	0.02

3M OCCUPATIONAL HEALTH & ENVIRONMENTAL SAFETY DIVISION
MONITOR BULLETIN X
November, 1990

Listed in the following table are the theoretical calculated sampling rates (SR) for halothane, enflurane and isoflurane (Forane). Also listed are recoveries (REC) using carbon disulfide for desorption, limits of detection (LOD) for our analysis lab procedure using a flame ionization detector (FID) and retention times (RT) using our lab procedure.

Our capillary column gas chromatography procedure involves simultaneous analysis on two columns (30m X .25mm I.D. X .25 um film thickness J&W DB WAX and DB5) with a temperature program of 3 min @ 40°C - 10°C/min - 30 min @ 180°C.

	Halothane	Isoflurane	Enflurane
SR	30.0	28.3	28.3
REC	.97	.75	.81
RT (DB5)	-	2.55	2.59
RT (DBWAX)	4.68	4.47	-
LOD (UG)	10.8	10.4	10.8

A minimum sampling time of approximately 90 min is required to obtain 10 ug at an air concentration of 0.5 ppm.

Lower LODs have been obtained with an electron capture detector (ECD) using isooctane for desorption and chromatography on a 30 m X .53 mm I.D. X 5 um film thickness J&W DB1 megabore column at 100°C isothermal. The recovery for halothane was 0.11. Contamination peaks from the OVM blank interfered with the isoflurane and enflurane peaks.

Methylene Chloride Passive Dosimeter Field Validation in a Single Component Atmosphere

The current Method used for collecting Methylene Chloride (MeCl2) samples is an active method which requires a Low Flow Sampling Pump and a 600 mg Medium Charcoal Tube. An alternative method, passive dosimeters, was evaluated for collecting MeCl2 samples. The passive dosimeter method has many benefits compared to the active method: the dosimeters can be used rapidly without requiring the pre-calibration of pumps, there will be less paper work with a passive dosimeter because pump calibration records will not be necessary, there will be less equipment required to collect samples, the procedure will be less cumbersome for the employee who's exposure is being evaluated because they will not be required to wear a pump with a hose and there will not be the possibility of a lost sample due to pump failure. However, before the passive dosimeters could replace the active method their use needed to be validated.

The MeCl2 Passive Dosimeter Field Validation Study was completed in January of 1995. Four passive dosimeter models and a new sorbent material from SKC were compared to the current active method, Medium Charcoal Tube. Ten individual field validations were performed, five for PEL validation and five for STEL validation. The Field Validations were performed under various temperatures, pressures and relative humidities as shown in Table 1. All Field validations were performed in CAPD Building R5/R6 were there was only one chemical component, MeCl2, present at significant amounts. The four models of passive dosimeters evaluated were; SKC series 575, 3M model #3520 and Assay Technology model 541 and 546. All passive dosimeters evaluated performed acceptably, however, the new sorbent material was inferior to the current active method. A summary of the results of the field validations is given in Appendix A.

Since all the models of passive dosimeters evaluated performed well, the recommendation of which model to use will be based on special characteristics of each style of dosimeter, ease of use and cost per dosimeter.

Each style of dosimeter had some special characteristics. The 3M Badge has two sections which work in a similar way as the backup section in tubes, if greater than 50% of the total mass collected is on the secondary section the sample is considered invalid. This feature would be useful in high concentration areas, however, it was not needed during this series of field validations. The Assay Technology dosimeters offered a choice between a high sampling dosimeter and a high capacity dosimeter. This option is useful for STEL sampling because the high sampling rate model assures the collection of a quantifiable amount of MeCl2 and for PEL sampling with the high capacity model which samples at a lower rate to avoid saturating the dosimeter. These dosimeters may also be re-usable when a new carbon wafer is placed in the dosimeter housing. The SKC series dosimeter was by far the easiest to desorb and analyze because of its single collection pad and internal desorption. The recommended shelf life of all dosimeters is given in Table 2. The cost per monitor is given in Table 3.

The SKC dosimeter is the least expensive, however, there is the possibility that Assay Technology will sell us the individual carbon wafer that can be placed in the re-usable housing of the dosimeter. This option is sure to be significantly less than the cost of the complete badge.

The SKC Series 575 is currently the recommended dosimeter of CIHL because of its ease of use and analysis and because of its reduced cost. This recommendation may change depending on the cost of the Assay Technology replacement carbon wafer.

Methylene Chloride Passive Dosimeter Field Validation

Table 1. Environmental Conditions During Field Validation.

Field Validation	Date	Atmospheric Pressure (mm HG)	Average Temperature (Celsius)	Average Relative Humidity (%)	Water Concentration (mg/m3)
PEL	9/26/94	746	14.3	60.7	7120
PEL	10/3/94	752	17.7	54.1	8190
PEL	10/17/94	750	20.4	58	9990
PEL	10/31/94	748	19.4	37.6	6040
PEL	11/7/94	759	21.2	23	4180
STEL	10/27/94	757	21.1	22.1	4010
STEL	11/2/94	756	31.2	19.2	6320
STEL	12/5/94	752	19.9	31.5	5390
STEL	12/14/94	748	21.8	15.8	3050
STEL	1/10/95	748	23.2	13.6	2790

Table 2. Recommended Shelf Life of Passive Dosimeters.

Dosimeter	Recomended Shelf Life
Assay Technology Model 541/546	12 months
3M Model #3520	18 months
SKC Series 575	21 months

Table 3. Cost for a single monitor.

Monitor	Cost/Monitor
Assay Technology Model 541/546	$13.50
3M Model #3520	$16.26
SKC Series 575	$10.80
Medium Charcoal Tube (a)	$6.14*

* Includes cost of pump and calibration.

(a)This value was determined based on the following assumptions and costs:

Cost of Pump per sample: ($425 Cost of Pump)/{(2 samples per week) x (52 weeks per year) x (5 year life of Pump)} = $0.82 per sample

Cost of Gilibrator per sample ($1000 Cost of Gilibrator)/{(50 samples per week) x (52 weeks per year) x (5 year life of Gilibrator)} = $0.08 per sample

Cost of Wages per sample ($30,000 Salary x 1.33 for fringe) = $39,900/year
($39,900 per year)/ {(2000 hrs per year) x (60 min per hour) =33.3 cents per minute x 10 min per sample = $3.33 per sample

Cost of 600 mg Charcoal Tube $1.91

Total Cost per Sample = (Cost of Pump + Cost of Gilibrator + Cost of Wages + Cost of Tube)
= ($0.82 + $0.08 + $3.33 + $1.91) = $6.14

Don Larsen, 3M OH+ES

February 2, 1995

Martin Harper SKC
Gus Manning Assay Technology
Bob Weber 3M

cc:

Mark Puskar Abbott Laboratories: CIHL
Elisabel Puskar Abbott Laboratories: CAPD
Jim Murphy Abbott Laboratories: CHS

FIELD VALIDATION OF PASSIVE DOSIMETERS FOR THE DETERMINATION OF EMPLOYEE EXPOSURES TO METHYLENE CHLORIDE IN PHARMACEUTICAL PRODUCTION FACILITIES

The Methylene Chloride Field Validation Study was completed in January of 1995. Enclosed for your review are the individual results of the ten field validations. Included with the results are the procedures followed to desorb the samples, a list of abbreviations, some of the calculations used to determine the results and a summary sheet for all ten validations showing the bias and accuracy of the various media as they compare to the Medium Charcoal Tube method. This information is being given to allow you the opportunity to interpret the raw data and submit suggested discussion topics and conclusions. We would also like your opinion on the possibility of performing one or two more field validations for the STEL portion of the study because of multiple results at the 100 ppm level. We look forward to your comments. If you are going to attend the Laboratory Accreditation Committee Meeting on February 12 please bring this information as Mark will attend and would like to discuss the results. If you have any questions or comments pleases feel free to contact Mark Puskar or myself.

Sincerely,

Kem A Charron

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Methylene Chloride Passive Dosimeter Field Validation Summary

Sample		Medium Charcoal Tube				Assay Passive Monitor				Carbon Molecular Sieve Tube				SKC Passive Monitor				3M Passive Monitor			
Type	Date	Mean (ppm)	Cv(%)	Bias(%)	Accuracy	Mean (ppm)	Cv(%)	Bias(%)	Accuracy	Mean (ppm)	Cv(%)	Bias(%)	Accuracy	Mean (ppm)	Cv(%)	Bias(%)	Accuracy	Mean (ppm)	Cv(%)	Bias(%)	Accuracy
PEL	10/17/94	0.9	14.4	0	28.8	1.0	8.74	11.1	28 6	1.0	15.2	11.1	41.5	1.0	8 83	11.1	28.8	0.8	8.14	-11.1	27.4
PEL	11/7/94	3.1	5.75	0	11.5	3.4	14.1	9.68	37.9	3.5	12	12.9	36.9	4.1	3.59	32.3	39.4	3.0	2.69	-3.23	8.61
PEL	10/3/94	14.8	1.1	0	2.20	13.5	1.76	-8.78	12.3	16.5	16.2	11.5	43.9	14.8	3.03	0 00	6.1	13.8	2.64	-6.76	12.0
PEL	9/26/94	28.9	1.37	0	2.74	27.5	1.63	-4.84	8.10	28.1	1.91	-2.77	6.59	28.0	3.17	-3.11	9.45	26.5	3.12	-8.30	14.5
PEL	10/31/94	62.7	2 6	0	5.20	59 0	2.51	-5.90	10 9	69.7	9.93	11.2	31.0	65.7	3.2	4.8	11.2	56 6	4.01	-9.73	17.7
Pooled Bias=				0.00				8.06				9.89				10.3				7.83	
Pooled Accuracy=					10.1				19.6				32.0				19.0				16.1
STEL	12/5/94	14.4	9.96	0	19.9	14.6	4.87	1.39	11.1	13.6	8.2	-5.56	22.0	15.8	5.66	9.72	21.0	14.1	4.16	-2.08	10.4
STEL	1/10/95	96.2	3.32	0	6 64	108	4.4	12.27	21.1	99.4	4.3	3.33	11.9	114	6.83	18.5	32.2	87.6	6.66	-8.94	22.3
STEL	11/2/94	101	31.4	0	62.8	106	25.9	4.95	56.8	92.1	28.1	-8.81	65.0	103	19.4	1.98	40.8	103	26.1	1.98	54.2
STEL	12/14/94	113	20.5	0	41.0	107	11.3	-5.31	27.9	104	24.4	-7.96	56.8	116	13.1	2 65	28.9	85 9	9.41	-24.0	42.8
STEL	10/27/94	357	5 31	0	10.6	394	5 57	10.36	21.5	357	6.54	0 00	13.1	413	6.05	15.7	27.8	345	6.17	-3.36	15.7
Pooled Bias=				0 00				6.86				6.41				9.71				8.07	
Pooled Accuracy=					28.2				27.7				33.7				30.1				29 1

Bias = ((Amount Found-Amount Known)/Amount Known) x 100. Amount Known=Reference Method, Medium Charcoal Tube

Accuracy= [2(CV)+|Bias|]

3M 110654

Methylen Chloride Passive Dosimeter Field Validation

DESORPTION OF SAMPLING MATERIALS

Medium Charcoal Tube (MCT) 600 mg

Desorption Efficiency: 100 %
Desorption solution: Carbon Disulfide (CS_2) with 5% Methanol (MeOH)

Desorption procedure: Add 2 mL of CS_2:MeOH to the front and back section of tube in seperate vials, immediatly reseal vial. Vortex mix the solution and place on counter for 30 minutes. After 30 min an aliquot is removed from the vial and placed in an autosampler vial for analysis.

SKC Anasorb Carbon Molecular Sieve (CMS) 150/75mg

Desorption Efficiency: 97.6 +/- 4.22% (n = 46)
Desorption solution: Carbon Disulfide (CS_2)

Desorption procedure: Add 2 mL of CS_2 to the front and back section of tube in seperate chilled vials. Mechanically agitae the vials for 30 minutes. An aliquot is removed from the vials and placed in an autosampler vial for analysis.

SKC Passive Sampler 575 Series

Desorption Efficiency: 96.0 +/- 4.3% **Sampling Rate:** 14.5 mL/min
Desorption solution: Carbon Disulfide (CS_2)

Desorption procedure: Add 2 mL of CS_2 to each monitor through the center port, immediatly reseal port. The monitors are agitaed for 30 minutes. An aliquot is removed from the monitor and placed in an autosampler vial for analysis.

Assay Technologies Personal Monitoring System Model 541 and 546

Desorption Efficiency: 92.0 %
Sampling Rate: Monitor 541= 7.57 mL/min Monitor 546= 1.89 mL/min
Desorption solution: Carbon Disulfide (CS_2)

Desorption procedure: Use forcepts, quickly remove the sample wafer from the plastic cavity, break the wafer into two pieces and place into a 7ml glass vial with an inert closure. Quickly add 1.0 mL of CS_2 to each vial. Agitate the vial continuously for 1 hr. An aliquot is removed from the 7 ml vial and placed in an autosampler vial for analysis.

3M Organic Vapor Monitors #3520 with Back-up Section

Desorption Efficiency: 90 % **Sampling Rate:** 37.9 mL/min
Desorption solution: Carbon Disulfide (CS_2)

Desorption procedure: Add 1.5 mL of CS_2 to each monitor through the center port, immediatly reseal port. The monitors are occasionally agitaed for 30 minutes. An aliquot is removed from the monitor and placed in an autosampler vial for analysis.

Methylene Chloride Passive Dosimeter Field Validation

Abreviations used on Results Sheets

MCT= Medium Charcoal Tube, 600 mg total weight
CMS= SKC Anasorb Carbon Molecular Sieve, 225 mg total weight
SKC= SKC Passive Sampler 575 Series
ASSAY= Assay Technologies Personal Monitoring System Model 541 and 546
3M= 3M Organic Vapor Monitor #3520 with Back-up Section

Calculations used for determining results

Equation 1

Concentration in ppm= (Total mcg)x(24.45)/(M.W. of MeCl2)x(Total Air Volume in L)

Equation 2

Total mcg for 3M Organic Vapor Monitors= (Wp+(2.2xWs))

Wp= mcg of MeCl2 on Primary Section. Ws= mcg of MeCl2 on Secondary Section.

SKC and Assay Monitor results were corrected for Pressure and Temperature by multiplying the Concentration by a PT correction factor. The correction factor was determined using *Equation 3*.

The 3M results were corrected according to the Table given in the "3M Organic Vapor Monit r #3500/3520 Analysis Guide".

Equation 3

$$PT = (Ta/Ts)^{1.5} (Ps/Pa)$$

Ta= Temperature in Kelvin at sampling area
Ts= Standard Temperature(298 Kelvin)
Pa= Pressure in mm Hg at sampling area
Ps= Standard Pressure(760 mm Hg)

Results for Methylene Chloride Passive Dosimeter Field Validation (Run # 1, PEL # 1, 9-26-94).

Active Samples

Pump ID	Sample ID	Pre-Cal (mL/min)	Post-Cal (mL/min)	Avg (mL/min)	Sample Time(min)	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Concentration (ppm)	
10374	1-MCT-A	101.3	100.95	101.13	480	48.54	1	4891	0	4891	2mL	29.0	
10377	1-MCT-B	100.6	101.1	100.85	480	48.41	1	4838	0	4838	2mL	28.8	
10375	1-MCT-C	97.36	97.72	97.54	480	46.82	1	4649	0	4649	2mL	28.6	MCT
10376	1-MCT-D	101.5	100.1	100.80	480	48.38	1	4852	11.4	4863	2mL	28.9	Average Conc.= 28.9
10372	1-MCT-E	97.03	94.84	95.94	480	46.05	1	4568	0	4568	2mL	28.6	Std. Dev.= 0.40
10378	1-MCT-F	100.5	100.9	100.70	480	48.34	1	4976	0	4976	2mL	29.6	C.V.= 1.37%
10389	1-MCT-BLANK	101.2	101.2	101.20	480	48.58	1	11.675	0	12	2mL	0.1	
10379	1-CMS-A	99.84	102.6	101.22	480	48.59	0.976	2436	2245	4795	2mL	28.4	
10380	1-CMS-B	97.01	99.91	98.46	480	47.26	0.976	3809	624	4542	2mL	27.7	
10426	1-CMS-C	97.57	98.71	98.14	480	47.11	0.976	3681	698	4487	2mL	27.4	CMS
10427	1-CMS-D	100.9	101.9	101.40	480	48.67	0.976	4047	649	4811	2mL	28.6	Average Conc.= 28.1
10428	1-CMS-E	98.61	99.9	99.26	480	47.64	0.976	3812	691	4614	2mL	27.9	Std. Dev.= 0.54
10429	1-CMS-F	100.7	100.9	100.80	480	48.38	0.976	4113	614	4843	2mL	28.8	C.V.= 1.91%
10430	1-CMS-BLANK	103.2	104.6	103.90	480	49.87	0.976	7.4	0	8	2mL	0.0	

Passive Dosimeters

Sample Type	Sample ID	Sampling Rate(mL/min)	Sampling Time	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Corrected Total [b]	Concentration (ppm)	T/P Corrected Conc. (ppm)	
SKC	1-001	14.5	480	6.96	0.96	610	[a]	635	2mL	635	26.3	27.2	
SKC	1-002	14.5	480	6.96	0.96	611	[a]	636	2mL	636	26.3	27.3	
SKC	1-003	14.5	480	6.96	0.96	621	[a]	647	2mL	647	26.8	27.7	SKC
SKC	1-004	14.5	480	6.96	0.96	622	[a]	648	2mL	648	26.8	27.8	Average Conc.= 28.0
SKC	1-005	14.5	480	6.96	0.96	639	[a]	666	2mL	666	27.6	28.5	Std. Dev.= 0.89
SKC	1-006	14.5	480	6.96	0.96	662	[a]	690	2mL	690	28.5	29.6	C.V.= 3.17%
SKC	1-BLANK	14.5	480	6.96	0.96	0	[a]	0	2mL	0	0.0	0.0	
ASSAY	T0061(Blk)	7.57	480	3.63	0.92	0	[a]	0	1mL	0	0.0	0	
ASSAY	T0052	7.57	480	3.63	0.92	604	[a]	657	1mL	328	26.0	27.0	
ASSAY	T0053	7.57	480	3.63	0.92	610	[a]	663	1mL	332	26.3	27.2	ASSAY
ASSAY	T0054	7.57	480	3.63	0.92	612	[a]	665	1mL	333	26.3	27.3	Average Conc.= 27.5
ASSAY	T0055	7.57	480	3.63	0.92	617	[a]	671	1mL	335	26.6	27.5	Std. Dev.= 0.45
ASSAY	T0057	7.57	480	3.63	0.92	633	[a]	688	1mL	344	27.3	28.3	C.V.= 1.63%
ASSAY	T0058	7.57	480	3.63	0.92	620	[a]	674	1mL	337	26.7	27.7	
3M	VK 03760C	37.9	480	18.19	0.9	1714	108	2168	1.5 mL	1626	25.7	26.2	
3M	VK 03563C	37.9	480	18.19	0.9	1724	97.4	2154	1.5 mL	1615	25.6	26.1	
3M	VK 03579C(Blk)	37.9	480	18.19	0.9	0	0	0	1.5 mL	0	0.0	0.0	3M
3M	VK 03515C	37.9	480	18.19	0.9	1884	76.8	2281	1.5 mL	1711	27.1	27.6	Average Conc.= 26.5
3M	VK 03652C	37.9	480	18.19	0.9	1717	99.5	2151	1.5 mL	1613	25.5	26.0	Std. Dev.= 0.83
3M	VK 03728C	37.9	480	18.19	0.9	1778	123	2276	1.5 mL	1707	27.0	27.6	C.V.= 3.12%
3M	VK 03769C	37.9	480	18.19	0.9	1733	81.1	2124	1.5 mL	1593	25.2	25.7	

[a] There is only one section to these samples.
[b] Corrected for desorption volume differences.

Temperature= 14.3 degrees Celsius
Pressure= 746 mm Hg

Results for Methylene Chloride Passive Dosimeter Field Validation (Run # 2, PEL #2, 10-3-94).

Active Samples

Pump ID	Sample ID	Pre-Cal (mL/min)	Post-Cal (mL/min)	Avg (mL/min)	Sample Time(min)	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Concentration (ppm)	
10374	2-MCT-A	19.72	20.56	20.14	480	9.67	1	500.9	0	501	2mL	14.9	
10377	2-MCT-B	19.81	19.98	19.90	480	9.55	1	492.6	0	493	2mL	14.8	
10375	2-MCT-C	20.61	20.57	20.59	480	9.88	1	501.2	0	501	2mL	14.6	MCT
10376	2-MCT-D	20.12	20.45	20.29	480	9.74	1	605.1	0	605	2mL	14.9	Average Conc.= 14.8
10372	2-MCT-E	20.47	20.59	20.53	480	9.86	1	512	0	512	2mL	15.0	Std. Dev.= 0.16
10378	2-MCT-F	19.86	20.11	19.99	480	9.59	1	487	0	487	2mL	14.6	C.V.= 1.10%
10389	2-MCT-BLANK	19.93	19.92	19.93	480	9.56	1	0	0	0	2mL	0.0	
10427	2-CMS-A	19.94	20	19.97	480	9.59	0.976	670	0	686	2mL	20.6	
10426	2-CMS-B	19.57	19.56	19.52	480	9.42	0.976	596.7	4.1	616	2mL	18.8	
10428	2-CMS-C	20.03	20.56	20.30	480	9.74	0.976	489	0	501	2mL	14.8	CMS
10430	2-CMS-D	20.08	20.06	20.07	480	9.63	0.976	473	7.8	493	2mL	14.7	Average Conc.= 16.5
10429	2-CMS-E	20.44	20.56	20.50	480	9.84	0.976	458	0	469	2mL	13.7	Std. Dev.= 2.68
10380	2-CMS-F	20.17	20.04	20.11	480	9.65	0.976	538	0	551	2mL	16.4	C.V.= 16.2%
10379	2-CMS-BLANK	20.74	20.67	20.71	480	9.94	0.976	0	0	0	2mL	0.0	

Passive Dosimeters

Sample Type	Sample ID	Sampling Rate(mL/min)	Sampling Time	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	*Corrected* Total [b]	*Concentration* (ppm)	*T/P Corrected* Conc. (ppm)	
SKC	2-001	14.5	480	6.96	0.96	342	[a]	356	2mL	356	14.7	15.1	
SKC	2-002	14.5	480	6.96	0.96	349	[a]	364	2mL	364	15.0	15.4	
SKC	2-003	14.5	480	6.96	0.96	333	[a]	347	2mL	347	14.3	14.7	SKC
SKC	2-004	14.5	480	6.96	0.96	328	[a]	342	2mL	342	14.1	14.5	Average Conc.= 14.8
SKC	2-005	14.5	480	6.96	0.96	326	[a]	340	2mL	340	14.0	14.4	Std. Dev.= 0.45
SKC	2-006	14.5	480	6.96	0.96	323	[a]	336	2mL	336	13.9	14.3	C.V.= 3.03%
SKC	2-BLANK	14.5	480	6.96	0.96	0	[a]	0	2mL	0	0.0	0.0	
ASSAY	U1010(Blank)	1.89	480	0.91	0.92	0	[a]	0	1mL	0	0.0	0	
ASSAY	U1001	1.89	480	0.91	0.92	77	[a]	84	1mL	42	13.3	13.5	
ASSAY	U1002	1.89	480	0.91	0.92	74.8	[a]	81	1mL	41	12.9	13.3	ASSAY
ASSAY	U1003	1.89	480	0.91	0.92	77.4	[a]	84	1mL	42	13.3	13.7	Average Conc.= 13.5
ASSAY	U1005	1.89	480	0.91	0.92	77.5	[a]	84	1mL	42	13.4	13.7	Std. Dev.= 0.24
ASSAY	U1008	1.89	480	0.91	0.92	77.1	[a]	84	1mL	42	13.3	13.7	C.V.= 1.78%
ASSAY	U1009	1.89	480	0.91	0.92	74.5	[a]	81	1mL	40	12.8	13.2	
3M	VK 03866C	37.9	480	18.19	0.9	1013	21.7	1179	1.5 mL	884	14.0	14.1	
3M	VK 03448C	37.9	480	18.19	0.9	960	20.3	1116	1.5 mL	837	13.2	13.4	
3M	VK 03817C	37.9	480	18.19	0.9	968.5	24.9	1137	1.5 mL	853	13.5	13.6	3M
3M	VK 03649C	37.9	480	18.19	0.9	1023	25.5	1199	1.5 mL	899	14.2	14.4	Average Conc.= 13.8
3M	VK 03514C	37.9	480	18.19	0.9	973	23.8	1139	1.5 mL	854	13.5	13.7	Std. Dev.= 0.36
3M	VK 03843C	37.9	480	18.19	0.9	977	24.6	1146	1.5 mL	859	13.6	13.7	C.V.= 2.64%
3M	VK 03897C	37.9	480	18.19	0.9	0	0	0	1.5 mL	0	0.0	0.0	

[a] There is only one section to these samples.
[b] Corrected for desorption volume differences.

Temperature= 17.7 degrees Celsius
Pressure= 752 mm Hg

Results for Methylene Chloride Passive Dosimeter Field Validation (Run # 2, PEL #2, 10-3-94).

Active Samples

Pump ID	Sample ID	Pre- Cal (mL/min)	Post-Cal (mL/min)	Avg (mL/min)	Sample Time(min)	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Concentration (ppm)	
10374	2-MCT-A	19.72	20.56	20.14	480	9.67	1	500.9	0	501	2mL	14.9	
10377	2-MCT-B	19.81	19.98	19.90	480	9.55	1	492.5	0	493	2mL	14.8	
10375	2-MCT-C	20.61	20.57	20.59	480	9.88	1	501.2	0	501	2mL	14.6	MCT
10376	2-MCT-D	20.12	20.45	20.29	480	9.74	1	505.1	0	505	2mL	14.9	Average Conc.= 14.8
10372	2-MCT-E	20.47	20.59	20.53	480	9.86	1	512	0	512	2mL	15.0	Std. Dev.= 0.16
10378	2-MCT-F	19.86	20.11	19.99	480	9.59	1	487	0	487	2mL	14.6	C.V.= 1.10%
10389	2-MCT-BLANK	19.93	19.92	19.93	480	9.56	1	0	0	0	2mL	0.0	
10427	2-CMS-A	19.94	20	19.97	480	9.59	0.976	670	0	686	2mL	20.6	
10426	2-CMS-B	19.67	19.56	19.62	480	9.42	0.976	596.7	4.1	616	2mL	18.8	
10428	2-CMS-C	20.03	20.56	20.30	480	9.74	0.976	489	0	601	2mL	14.8	CMS
10430	2-CMS-D	20.08	20.06	20.07	480	9.63	0.976	473	7.8	493	2mL	14.7	Average Conc.= 16.5
10429	2-CMS-E	20.44	20.55	20.50	480	9.84	0.976	458	0	469	2mL	13.7	Std. Dev.= 2.68
10380	2-CMS-F	20.17	20.04	20.11	480	9.65	0.976	538	0	551	2mL	16.4	C.V.= 16.2%
10379	2-CMS-BLANK	20.74	20.67	20.71	480	9.94	0.976	0	0	0	2mL	0.0	

Passive Dosimeters

Sample Type	Sample ID	Sampling Rate(mL/min)	Sampling Time	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Corrected Total [b]	Concentration (ppm)	T/P Corrected Conc. (ppm)	
SKC	2-001	14.5	480	6.96	0.96	342	[a]	356	2mL	356	14.7	15.1	
SKC	2-002	14.5	480	6.96	0.96	349	[a]	364	2mL	364	15.0	15.4	
SKC	2-003	14.5	480	6.96	0.96	333	[a]	347	2mL	347	14.3	14.7	SKC
SKC	2-004	14.5	480	6.96	0.96	328	[a]	342	2mL	342	14.1	14.5	Average Conc.= 14.8
SKC	2-005	14.5	480	6.96	0.96	326	[a]	340	2mL	340	14.0	14.4	Std. Dev.= 0.45
SKC	2-006	14.5	480	6.96	0.96	323	[a]	336	2mL	336	13.9	14.3	C.V.= 3.03%
SKC	2-BLANK	14.5	480	6.96	0.96	0	[a]	0	2mL	0	0.0	0.0	
ASSAY	U1010(Blank)	1.89	480	0.91	0.92	0	[a]	0	1mL	0	0.0	0	
ASSAY	U1001	1.89	480	0.91	0.92	77	[a]	84	1mL	42	13.3	13.6	
ASSAY	U1002	1.89	480	0.91	0.92	74.8	[a]	81	1mL	41	12.9	13.3	ASSAY
ASSAY	U1003	1.89	480	0.91	0.92	77.4	[a]	84	1mL	42	13.3	13.7	Average Conc.= 13.5
ASSAY	U1005	1.89	480	0.91	0.92	77.5	[a]	84	1mL	42	13.4	13.7	Std. Dev.= 0.24
ASSAY	U1008	1.89	480	0.91	0.92	77.1	[a]	84	1mL	42	13.3	13.7	C.V.= 1.78%
ASSAY	U1009	1.89	480	0.91	0.92	74.5	[a]	81	1mL	40	12.8	13.2	
3M	VK 03866C	37.9	480	18.19	0.9	1013	21.7	1179	1.5 mL	884	14.0	14.1	
3M	VK 03448C	37.9	480	18.19	0.9	960	20.3	1116	1.5 mL	837	13.2	13.4	
3M	VK 03817C	37.9	480	18.19	0.9	968.5	24.9	1137	1.5 mL	853	13.5	13.6	3M
3M	VK 03649C	37.9	480	18.19	0.9	1023	25.5	1199	1.5 mL	899	14.2	14.4	Average Conc.= 13.8
3M	VK 03514C	37.9	480	18.19	0.9	973	23.8	1139	1.5 mL	854	13.5	13.7	Std. Dev.= 0.36
3M	VK 03843C	37.9	480	18.19	0.9	977	24.6	1146	1.5 mL	859	13.6	13.7	C.V.= 2.64%
3M	VK 03897C	37.9	480	18.19	0.9	0	0	0	1.5 mL	0	0.0	0.0	

[a] There is only one section to these samples.
[b] Corrected for desorption volume differences.

Temperature= 17.7 degrees Celsius
Pressure= 762 mm Hg

3M 110659

Results for Methylene Chloride Passive Dosimeter Field Validation (Run #3, PEL #3, 10-17-94).

Active Samples

Pump ID	Sample ID	Pre-Cal (mL/min)	Post-Cal (mL/min)	Avg (mL/min)	Sample Time(min)	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Concentration (ppm)	
10374	3-MCT-A	20.62	19.95	20.29	480	9.74	1	37.6	0	38	2mL	1.1	
10377	3-MCT-B	20	19.72	19.86	480	9.53	1	31.4	0	31	2mL	0.9	
10375	3-MCT-C	20.67	20.42	20.55	480	9.86	1	28.3	0	28	2mL	0.8	MCT
10376	3-MCT-D	20.47	20.4	20.44	480	9.81	1	26.8	0	27	2mL	0.8	Average Conc.= 0.9
10372	3-MCT-E	20.79	20.37	20.58	480	9.88	1	26.6	0	27	2mL	0.8	Std. Dev.= 0.13
10378	3-MCT-F	20.27	20.28	20.28	480	9.73	1	28.9	0	29	2mL	0.9	C.V.= 14.4%
10389	3-MCT-BLANK	19.9	19.62	19.76	480	9.48	1	2.78	0	3	2mL	0.1	
10426	3-CMS-A	19.56	18.25	18.91	480	9.07	0.976	33.8	0	35	2mL	1.1	
10430	3-CMS-B	20.36	20.44	20.40	480	9.79	0.976	41.2	0	42	2mL	1.2	
10429	3-CMS-C	20.29	20.03	20.16	480	9.68	0.976	30	0	31	2mL	0.9	CMS
10428	3-CMS-D	20.88	20.96	20.93	480	10.05	0.976	30	0	31	2mL	0.9	Average Conc.= 1.0
10380	3-CMS-E	19.89	19.66	19.78	480	9.49	0.976	27.3	0	28	2mL	0.8	Std. Dev.= 0.15
10427	3-CMS-F	20.9	20.87	20.89	480	10.02	0.976	32.8	0	34	2mL	1.0	C.V.= 15.2%
10379	3-CMS-BLANK	20.66	20.52	20.59	480	9.88	0.976	5.78	0	6	2mL	0.2	

Passive Dosimeters

Sample Type	Sample ID	Sampling Rate(mL/min)	Sampling Time	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Corrected Total [b]	Concentration (ppm)	T/P Corrected Conc. (ppm)	
SKC	3-001	14.5	480	6.96	0.96	26.1	[a]	27	2mL	27	1.1	1.1	
SKC	3-002	14.5	480	6.96	0.96	22.6	[a]	24	2mL	24	1.0	1.0	
SKC	3-003	14.5	480	6.96	0.96	23.6	[a]	25	2mL	25	1.0	1.0	SKC
SKC	3-004	14.5	480	6.96	0.96	21.2	[a]	22	2mL	22	0.9	0.9	Average Conc.= 1.0
SKC	3-005	14.5	480	6.96	0.96	22.3	[a]	23	2mL	23	1.0	1.0	Std. Dev.= 0.09
SKC	3-006	14.5	480	6.96	0.96	20.4	[a]	21	2mL	21	0.9	0.9	C.V.= 8.83%
SKC	3-BLANK	14.5	480	6.96	0.96	5.26	[a]	5	2mL	5	0.2	0.2	
ASSAY	U1044(Blank)	1.89	480	0.91	0.92	0	[a]	0	1mL	0	0.0	0.0	
ASSAY	U1045	1.89	480	0.91	0.92	5.2	[a]	6	1mL	3	0.9	0.9	
ASSAY	U1046	1.89	480	0.91	0.92	5.97	[a]	6	1mL	3	1.0	1.0	ASSAY
ASSAY	U1047	1.89	480	0.91	0.92	5.26	[a]	6	1mL	3	0.9	0.9	Average Conc.= 1.0
ASSAY	U1048	1.89	480	0.91	0.92	6.3	[a]	7	1mL	3	1.1	1.1	Std. Dev.= 0.09
ASSAY	U1049	1.89	480	0.91	0.92	6.2	[a]	7	1mL	3	1.1	1.1	C.V.= 8.74%
ASSAY	U1050	1.89	480	0.91	0.92	5.35	[a]	6	1mL	3	0.9	0.9	
3M	VK 04157C	37.9	480	18.19	0.9	68.3	0	76	1.5 mL	57	0.9	0.9	
3M	VK 03670C	37.9	480	18.19	0.9	63	0	70	1.5 mL	53	0.8	0.8	
3M	VK 04108C	37.9	480	18.19	0.9	61.2	0	68	1.5 mL	51	0.8	0.8	3M
3M	VK 04043C	37.9	480	18.19	0.9	56.9	0	63	1.5 mL	47	0.8	0.8	Average Conc.= 0.8
3M	VK 03948C	37.9	480	18.19	0.9	54.8	0	61	1.5 mL	46	0.7	0.7	Std. Dev.= 0.07
3M	VK 03954C	37.9	480	18.19	0.9	57.7	0	64	1.5 mL	48	0.8	0.8	C.V.= 8.14%
3M	VK 03844C BLK	37.9	480	18.19	0.9	8.72	0	10	1.5 mL	7	0.1	0.1	

[a] There is only one section to these samples.
[b] Corrected for desorption volume differences.

Temperature= 20.4 degrees Celsius
Pressure= 760 mm Hg

Results for Methylene Chloride Passive Dosimeter Field Validation (Run #4 STEL # 1, 10-27-94).

Active Samples

Pump ID	Sample ID	Pre- Cal (mL/min)	Post-Cal (mL/min)	Avg (mL/min)	Sample Time(min)	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Concentration (ppm)	
10374	4-MCT-A	100.6	101.1	100.85	15	1.51	1	1940	0	1940	2mL	369.1	
10377	4-MCT-B	101	100.9	100.95	15	1.51	1	2004	0	2004	2mL	380.9	
10375	4-MCT-C	101.7	101.1	101.40	15	1.52	1	1801	0	1801	2mL	340.8	MCT
10376	4-MCT-D	100.1	101.3	100.70	15	1.51	1	1945	0	1945	2mL	370.7	Average Conc.= 357
10372	4-MCT-E	101.3	101.4	101.35	15	1.52	1	1762	0	1762	2mL	333.6	Std. Dev.= 19.0
10378	4-MCT-F	99.71	99.91	99.81	15	1.50	1	1810	0	1810	2mL	348.0	C.V.= 5.31%
10391	4-MCT-BLANK	100.5	100.6	100.55	15	1.51	1	0	0	0	2mL	0.0	
10426	4-CMS-A	99.49	97.11	98.30	15	1.47	0.976	1810	0	1855	2mL	362.0	
10430	4-CMS-B	101.3	101.7	101.50	15	1.52	0.976	2014	0	2064	2mL	390.1	
10429	4-CMS-C	99.31	99.46	99.39	15	1.49	0.976	1674	0	1715	2mL	331.2	CMS
10428	4-CMS-D	101.9	102.2	102.05	15	1.53	0.976	1871	0	1917	2mL	360.5	Average Conc.= 357
10380	4-CMS-E	101.1	101.8	101.45	15	1.52	0.976	1702	0	1744	2mL	329.9	Std. Dev.= 23.4
10427	4-CMS-F	100.8	100.8	100.80	15	1.51	0.976	1901	0	1948	2mL	370.8	C.V.= 6.64%
10379	4-CMS-BLANK	100.3	100	100.15	15	1.50	0.976	0	0	0	2mL	0.0	

Passive Dosimeters

Sample Type	Sample ID	Sampling Rate(mL/min)	Sampling Time	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Corrected Total [b]	Concentration (ppm)	T/P Corrected Conc. (ppm)	
SKC	4-001	14.5	15	0.22	0.96	321	[a]	334	2mL	334	442.5	449.7	
SKC	4-002	14.5	15	0.22	0.96	277	[a]	289	2mL	289	381.9	388.0	
SKC	4-003	14.5	15	0.22	0.96	305	[a]	318	2mL	318	420.5	427.3	SKC
SKC	4-004	14.5	15	0.22	0.96	303	[a]	316	2mL	316	417.7	424.5	Average Conc.= 413
SKC	4-005	14.5	15	0.22	0.96	279	[a]	291	2mL	291	384.6	390.8	Std. Dev.= 25.0
SKC	4-006	14.5	15	0.22	0.96	282	[a]	294	2mL	294	388.8	395.0	C.V.= 6.05%
SKC	4-BLANK	14.5	15	0.22	0.96	0	[a]	0	2mL	0	0.0	0.0	
ASSAY	T0141(Blank)	7.57	15	0.11	0.92	0	[a]	0	1mL	0	0.0	0	
ASSAY	T0144	7.57	15	0.11	0.92	289	[a]	314	1mL	157	398.2	404.6	
ASSAY	T0145	7.57	15	0.11	0.92	292	[a]	317	1mL	159	402.3	408.8	ASSAY
ASSAY	T0146	7.57	15	0.11	0.92	301	[a]	327	1mL	164	414.7	421.4	Average Conc.= 394
ASSAY	T0147	7.57	15	0.11	0.92	271	[a]	295	1mL	147	373.4	379.4	Std. Dev.= 22.0
ASSAY	T0148	7.57	15	0.11	0.92	258	[a]	280	1mL	140	355.6	361.2	C.V.= 6.57%
ASSAY	T0149	7.57	15	0.11	0.92	277	[a]	301	1mL	151	381.6	387.8	
3M	VK 03788C	37.9	15	0.57	0.9	870	0	967	1.5 mL	725	367.1	370.8	
3M	VK 03663C	37.9	15	0.57	0.9	869	0	966	1.5 mL	724	366.7	370.3	
3M	VK 03692C	37.9	15	0.57	0.9	813	0	903	1.5 mL	678	343.0	346.5	3M
3M	VK 03715C	37.9	15	0.57	0.9	753	0	837	1.5 mL	628	317.7	320.9	Average Conc.= 345
3M	VK 03653C	37.9	15	0.57	0.9	790	0	878	1.5 mL	658	333.3	336.7	Std. Dev.= 21.3
3M	VK 03769C	37.9	15	0.57	0.9	768	0	853	1.5 mL	640	324.1	327.3	C.V.= 6.17%
3M	VK 03754C BLK	37.9	15	0.57	0.9	0	0	0	1.5 mL	0	0.0	0.0	

[a] There is only one section to these samples.
[b] Corrected for desorption volume differences.

Temperature= 21.1 degrees Celsius
Pressure= 757 mm Hg

Results for Methylene Chloride Passive Dosimeter Field Validation (Run # 5, PEL # 4, 10-31-94).

Active Samples

Pump ID	Sample ID	Pre- Cal (mL/min)	Post-Cal (mL/min)	Avg (mL/min)	Sample Time(min)	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Concentration (ppm)	
10374	5-MCT-A	19.83	19.49	19.66	480	9.44	1	2125	0	2125	2mL	64.8	
10377	5-MCT-B	19.76	20.87	20.32	480	9.75	1	2050	0	2050	2mL	60.5	
10375	5-MCT-C	20.33	19.97	20.15	480	9.67	1	2102	0	2102	2mL	62.6	MCT
10376	5-MCT-D	20.5	20.88	20.69	480	9.93	1	2160	0	2160	2mL	62.6	Average Conc.= 62.7
10372	5-MCT-E	20.33	19.63	19.98	480	9.59	1	2143	0	2143	2mL	64.3	Std. Dev.= 1.63
10378	5-MCT-F	20.14	20.23	20.19	480	9.69	1	2071	0	2071	2mL	61.6	C.V.= 2.60%
10391	5-MCT-BLANK	20.62	20.43	20.53	480	9.85	1	1	0	1	2mL	0.0	
10426	5-CMS-A	19.78	19.16	19.47	480	9.35	0.976	2179	0	2233	2mL	68.8	
10427	5-CMS-B	20.25	20.33	20.29	480	9.74	0.976	2496	0	2557	2mL	75.6	
10429	5-CMS-C	20.11	20.48	20.30	480	9.74	0.976	2160	0	2213	2mL	65.4	CMS
10428	5-CMS-D	20.2	21.85	21.03	480	10.09	0.976	2245	0	2300	2mL	65.6	Average Conc.= 69.7
10430	5-CMS-E	19.83	20.19	20.01	480	9.60	0.976	2623	0	2688	2mL	80.5	Std. Dev.= 6.92
10380	5-CMS-F	20.64	20.72	20.68	480	9.93	0.976	2105	0	2167	2mL	62.5	C.V.= 9.93%
10379	5-CMS-BLANK	20.17	20.39	20.28	480	9.73	0.976	1	0	1	2mL	0.0	

Passive Dosimeters

Sample Type	Sample ID	Sampling Rate(mL/min)	Sampling Time	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Corrected Total [b]	Concentration (ppm)	T/P Corrected Conc. (ppm)	
SKC	5-001	14.5	480	6.96	0.96	1539	[a]	1603	2mL	1603	66.3	67.1	
SKC	5-002	14.5	480	6.96	0.96	1510	[a]	1573	2mL	1573	65.1	65.9	
SKC	5-003	14.5	480	6.96	0.96	1433	[a]	1493	2mL	1493	61.7	62.5	SKC
SKC	5-004	14.6	480	6.96	0.96	1568	[a]	1633	2mL	1633	67.6	68.4	Average Conc.= 65.7
SKC	5-005	14.5	480	6.96	0.96	1515	[a]	1578	2mL	1578	65.3	66.1	Std. Dev.= 2.10
SKC	5-006	14.5	480	6.96	0.96	1471	[a]	1532	2mL	1532	63.4	64.2	C.V.= 3.20%
SKC	6-BLANK	14.6	480	6.96	0.96	1	[a]	1	2mL	1	0.0	0.0	
ASSAY	U1004(Blank)	1.89	480	0.91	0.92	0	[a]	0	1mL	0	0.0	0.0	
ASSAY	U1006	1.89	480	0.91	0.92	331	[a]	360	1mL	180	57.1	57.8	
ASSAY	U1011	1.89	480	0.91	0.92	333	[a]	362	1mL	181	57.4	58.1	ASSAY
ASSAY	U1018	1.89	480	0.91	0.92	353	[a]	384	1mL	192	60.9	61.6	Average Conc.= 59.0
ASSAY	U1019	1.89	480	0.91	0.92	335	[a]	364	1mL	182	57.8	58.5	Std. Dev.= 1.48
ASSAY	U1041	1.89	480	0.91	0.92	342	[a]	372	1mL	186	59.0	59.7	C.V.= 2.51%
ASSAY	U1043	1.89	480	0.91	0.92	332	[a]	361	1mL	180	57.3	58.0	
3M	VK 03941C	37.9	480	18.19	0.9	3628	248	4637	1.5 mL	3478	55.0	55.6	
3M	VK 03904C	37.9	480	18.19	0.9	3740	268	4811	1.5 mL	3608	57.1	57.7	
3M	VK 03992C	37.9	480	18.19	0.9	3506	332	4707	1.5 mL	3530	55.9	56.4	3M
3M	VK 03963C	37.9	480	18.19	0.9	3466	248	4457	1.5 mL	3343	62.9	53.4	Average Conc.= 56.6
3M	VK 03718C	37.9	480	18.19	0.9	3519	325	4704	1.5 mL	3528	55.8	56.4	Std. Dev.= 2.27
3M	VK 03970C	37.9	480	18.19	0.9	3905	282	5028	1.5 mL	3771	59.7	60.3	C.V.= 4.01%
3M	VK 03598C BL	37.9	480	18.19	0.9	0	0	0	1.5 mL	0	0.0	0.0	

[a] There is only one section to these samples.
[b] Corrected for desorption volume differences.

Temperature= 19.4 degrees Celsius
Pressure= 748 mm Hg

Results for Methylene Chloride Passive Dosimeter Field Validation (Run #6 STEL # 2, 11-2-94).

Active Samples

Pump ID	Sample ID	Pre-Cal (mL/min)	Post-Cal (mL/min)	Avg (mL/min)	Sample Time(min)	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Concentration (ppm)	
10374	6-MCT-A	100.8	100.9	100.85	15	1.51	1	609	0	609	2mL	116.9	
10377	6-MCT-B	100.5	101	100.75	15	1.51	1	347	0	347	2mL	66.1	
10375	6-MCT-C	100.1	99.62	99.86	15	1.50	1	493	0	493	2mL	94.7	MCT
10376	6-MCT-D	101.5	100.96	101.23	15	1.52	1	456	0	456	2mL	86.4	Average Conc.= 100.6
10372	6-MCT-E	99.97	99.16	99.57	15	1.49	1	809	0	809	2mL	155.9	Std. Dev.= 31.56
10378	6-MCT-F	100.2	99.62	99.91	15	1.50	1	440	0	440	2mL	84.5	C.V.= 31.4%
10391	6-MCT-BLANK	100.9	100.8	100.85	15	1.51	1	3.3	0	3	2mL	0.6	
10379	6-CMS-A	100.1	100.5	100.30	15	1.50	0.976	602	0	614	2mL	98.4	
10380	6-CMS-B	100.2	100.4	100.30	15	1.50	0.976	336	0	344	2mL	65.9	
10426	6-CMS-C	100.1	99.55	99.83	15	1.50	0.976	458	0	469	2mL	90.2	CMS
10427	6-CMS-D	101.2	100.9	101.05	15	1.52	0.976	406	0	416	2mL	79.0	Average Conc.= 92.1
10428	6-CMS-E	100	99.52	99.76	15	1.50	0.976	710	0	727	2mL	139.9	Std. Dev.= 25.89
10429	6-CMS-F	101.4	101.1	101.25	15	1.52	0.976	409	0	419	2mL	79.4	C.V.= 28.1%
10430	6-CMS-BLANK	99.74	99.73	99.74	15	1.50	0.976	8.08	0	8	2mL	1.6	

Passive Dosimeters

Sample Type	Sample ID	Sampling Rate(mL/min)	Sampling Time	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Corrected Total [b]	Concentration (ppm)	T/P Corrected Conc. (ppm)	
SKC	6-001	14.5	15	0.22	0.96	71.2	[a]	74	2mL	74	98.2	95.0	
SKC	6-002	14.5	15	0.22	0.96	94.9	[a]	99	2mL	99	130.8	126.6	
SKC	6-003	14.5	15	0.22	0.96	94.4	[a]	98	2mL	98	130.1	125.9	SKC
SKC	6-004	14.5	15	0.22	0.96	61.2	[a]	64	2mL	64	84.4	81.6	Average Conc.= 103.1
SKC	6-005	14.5	15	0.22	0.96	62.6	[a]	65	2mL	65	86.3	83.5	Std. Dev.= 19.95
SKC	6-006	14.5	15	0.22	0.96	79.3	[a]	83	2mL	83	109.3	105.8	C.V.= 19.4%
SKC	6-BLANK	14.5	15	0.22	0.96	0	[a]	0	2mL	0	0.0	0.0	
ASSAY	T-Blk	7.57	15	0.11	0.92	0	[a]	0	1mL	0	0.0	0.0	
ASSAY	T0059	7.57	15	0.11	0.92	92.4	[a]	100	1mL	50	127.3	123.2	
ASSAY	T0060	7.57	15	0.11	0.92	110	[a]	120	1mL	60	161.5	146.6	ASSAY
ASSAY	T0098	7.57	15	0.11	0.92	57.1	[a]	62	1mL	31	78.7	76.1	Average Conc.= 105.6
ASSAY	T0099	7.57	15	0.11	0.92	81.9	[a]	89	1mL	45	112.8	109.2	Std. Dev.= 27.37
ASSAY	T0100	7.57	15	0.11	0.92	76.6	[a]	83	1mL	42	105.4	102.0	C.V.= 25.9%
ASSAY	T0142	7.57	15	0.11	0.92	28.7	[a]	31	2mL	31	79.1	76.3	
3M	VK 03544C	37.9	15	0.57	0.9	350	0	389	1.5 mL	292	147.7	146.2	
3M	VK 03545C	37.9	15	0.57	0.9	223	0	248	1.5 mL	186	94.1	93.2	
3M	VK 03625C	37.9	15	0.57	0.9	232	0	258	1.5 mL	193	97.9	96.9	3M
3M	VK 03673C	37.9	15	0.57	0.9	297	0	330	1.5 mL	248	125.3	124.1	Average Conc.= 103.2
3M	VK 03674C	37.9	15	0.57	0.9	175	0	194	1.5 mL	146	73.8	73.1	Std. Dev.= 26.98
3M	VK 03716C	37.9	15	0.57	0.9	205	0	228	1.5 mL	171	86.5	85.6	C.V.= 26.1%
3M	VK 03474C BLK	37.9	15	0.57	0.9	0	0	0	1.5 mL	0	0.0	0.0	

[a] There is only one section to these samples.
[b] Corrected for desorption volume differences.

Temperature= 31.2 degrees Celsius
Pressure= 756 mm Hg

3M 110663

Results for Methylene Chloride Passive Dosimeter Field Validation (Run # 7, PEL # 5, 11-07-94).

Active Samples

Pump ID	Sample ID	Pre- Cal (mL/min)	Post-Cal (mL/min)	Avg (mL/min)	Sample Time(min)	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Concentration (ppm)	
10374	7-MCT-A	19.77	20.46	20.12	480	9.66	1	110	0	110	2mL	3.3	
10377	7-MCT-B	20.34	20.74	20.54	480	9.86	1	108	0	108	2mL	3.2	
10375	7-MCT-C	19.88	19.14	19.51	480	9.36	1	94.7	0	95	2mL	2.9	MCT
10376	7-MCT-D	20.16	19.82	19.99	480	9.59	1	105	0	105	2mL	3.2	Average Conc.= 3.1
10372	7-MCT-E	20.31	16.35	18.33	480	8.80	1	88.3	0	88	2mL	2.9	Std. Dev.= 0.18
10378	7-MCT-F	20.05	19.81	19.93	480	9.57	1	110	0	110	2mL	3.3	C.V.= 5.75%
10391	7-MCT-BLANK	20.33	20.12	20.23	480	9.71	1	0	0	0	2mL	0.0	
10380	7-CMS-A	20.73	20.92	20.83	480	10.00	0.976	102	0	105	2mL	3.0	
10426	7-CMS-B	19.7	17.63	18.67	480	8.96	0.976	129	0	132	2mL	4.2	
10427	7-CMS-C	19.83	20.14	19.99	480	9.69	0.976	111	0	114	2mL	3.4	CMS
10428	7-CMS-D	20.7	20.5	20.60	480	9.89	0.976	112	0	115	2mL	3.3	Average Conc.= 3.5
10429	7-CMS-E	20.03	20.59	20.31	480	9.75	0.976	111	0	114	2mL	3.4	Std. Dev.= 0.41
10430	7-CMS-F	20.27	20.42	20.35	480	9.77	0.976	111	0	114	2mL	3.4	C.V.= 12.0%
10379	7-CMS-BLANK	19.96	19.72	19.84	480	9.52	0.976	3.23	0	3	2mL	0.1	

Passive Dosimeters

Sample Type	Sample ID	Sampling Rate(mL/min)	Sampling Time	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Corrected Total [b]	Concentration (ppm)	T/P Corrected Conc. (ppm)	
SKC	7-001	14.5	480	6.96	0.96	89.8	[a]	94	2mL	94	3.9	3.9	
SKC	7-002	14.5	480	6.96	0.96	88.7	[a]	92	2mL	92	3.8	3.9	
SKC	7-003	14.5	480	6.96	0.96	95.7	[a]	100	2mL	100	4.1	4.2	SKC
SKC	7-004	14.5	480	6.96	0.96	96.5	[a]	101	2mL	101	4.2	4.2	Average Conc.= 4.1
SKC	7-005	14.5	480	6.96	0.96	90.8	[a]	95	2mL	95	3.9	4.0	Std. Dev.= 0.15
SKC	7-006	14.5	480	6.96	0.96	94.7	[a]	99	2mL	99	4.1	4.2	C.V.= 3.59%
SKC	7-BLANK	14.5	480	6.96	0.96	0	[a]	0	2mL	0	0.0	0.0	
ASSAY	U1031(Blank)	1.89	480	0.91	0.92	0	[a]	0	1mL	0	0.0	0.0	
ASSAY	U1032	1.89	480	0.91	0.92	22.7	[a]	25	1mL	12	3.9	4.0	
ASSAY	U1033	1.89	480	0.91	0.92	16.6	[a]	18	1mL	9	2.9	2.9	ASSAY
ASSAY	U1034	1.89	480	0.91	0.92	15.7	[a]	17	1mL	9	2.7	2.8	Average Conc.= 3.4
ASSAY	U1035	1.89	480	0.91	0.92	21.1	[a]	23	1mL	11	3.6	3.7	Std. Dev.= 0.48
ASSAY	U1036	1.89	480	0.91	0.92	19.7	[a]	21	1mL	11	3.4	3.5	C.V.= 14.1%
ASSAY	U1037	1.89	480	0.91	0.92	20.8	[a]	23	1mL	11	3.6	3.7	
3M	VK 03567C	37.9	480	18.19	0.9	228	0	253	1.5 mL	190	3.0	3.0	
3M	VK 03570C	37.9	480	18.19	0.9	233	0	259	1.5 mL	194	3.1	3.1	
3M	VK 03834C	37.9	480	18.19	0.9	221	0	246	1.5 mL	184	2.9	2.9	3M
3M	VK 03853C	37.9	480	18.19	0.9	220	0	244	1.5 mL	183	2.9	2.9	Average Conc.= 3.0
3M	VK 03862C	37.9	480	18.19	0.9	233	0	259	1.5 mL	194	3.1	3.1	Std. Dev.= 0.08
3M	VK 03864C	37.9	480	18.19	0.9	233	0	259	1.5 mL	194	3.1	3.1	C.V.= 2.69%
3M	VK 03526C BLK	37.9	480	18.19	0.9	5.67	0	6	1.5 mL	5	0.1	0.1	

[a] There is only one section to these samples.
[b] Corrected for desorption volume differences.

Temperature= 21.2 degrees Celsius
Pressure= 759 mm Hg

3M 110664

Results for Methylene Chloride Passive Dosimeter Field Validation (Run # 8, STEL # 3, 12-5-94).

Active Samples

Pump ID	Sample ID	Pre- Cal (mL/min)	Post-Cal (mL/min)	Avg (mL/min)	Sample Time(min)	Total Vol (L)	Desorptio Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Concentration (ppm)	
10374	8-MCT-A	102.1	100.5	101.30	15	1.52	1	79.3	0	79	2mL	15.0	
10375	8-MCT-B	102.1	100.3	101.20	15	1.52	1	76	0	76	2mL	14.2	
10376	8-MCT-C	103.2	101.4	102.30	15	1.53	1	69.2	0	69	2mL	13.0	MCT
10377	8-MCT-D	98.71	98.73	98.72	15	1.48	1	87.3	0	87	2mL	17.0	Average Conc.= 14.4
10378	8-MCT-E	104.1	103.5	103.80	15	1.56	1	74.2	0	74	2mL	13.7	Std. Dev.= 1.44
10379	8-MCT-F	101.1	99.19	100.15	15	1.50	1	70.5	0	71	2mL	13.6	C.V.= 9.95%
3260	8-MCT-BLANK	98.47	99.4	98.94	15	1.48	1	0	0	0	2mL	0.0	
10391	8-CMS-A	98.6	98.16	98.38	15	1.48	0.976	76.7	0	78	2mL	15.1	
10429	8-CMS-B	97.5	96.95	96.73	15	1.46	0.976	63.9	0	65	2mL	13.0	
10426*	8-CMS-C*	98.6	102.5	100.55	15	1.51	0.976	9.69	0	10	2mL	1.9	CMS
10428	8-CMS-D	100.5	100.1	100.30	15	1.50	0.976	73.6	0	75	2mL	14.4	Average Conc.= 13.6
10380	8-CMS-E	101.4	101	101.20	15	1.62	0.976	68.6	0	70	2mL	13.3	Std. Dev.= 1.12
10389	8-CMS-F	98.3	97.13	97.72	15	1.47	0.976	61.4	0	63	2mL	12.4	C.V.= 8.2%
10430	8-CMS-BLANK	99.17	96.72	97.95	15	1.47	0.976	0	0	0	2mL	0.0	

* This pump faulted out during the run.

Passive Dosimeters

Sample Type	Sample ID	Sampling Rate(mL/min)	Sampling Time	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Corrected Total [b]	Concentration (ppm)	T/P Corrected Conc. (ppm)	
SKC	8-001	14.5	15	0.2175	0.96	12.2	[a]	13	2mL	13	16.8	17.1	
SKC	8-002	14.5	15	0.2175	0.96	11.2	[a]	12	2mL	12	15.4	15.7	
SKC	8-003	14.5	15	0.2175	0.96	11.4	[a]	12	2mL	12	15.7	16.0	SKC
SKC	8-004	14.5	15	0.2175	0.96	11.3	[a]	12	2mL	12	15.6	15.8	Average Conc.= 15.8
SKC	8-005	14.5	15	0.2175	0.96	10.2	[a]	11	2mL	11	14.1	14.3	Std. Dev.= 0.89
SKC	8-006	14.5	15	0.2175	0.96	11.3	[a]	12	2mL	12	15.6	15.8	C.V.= 5.66%
SKC	8-BLANK	14.5	15	0.2176	0.96	0	[a]	0	2mL	0	0.0	0.0	
ASSAY	T0047(Blank)	7.57	15	0.11	0.92	0	[a]	0	1mL	0	0.0	0.0	
ASSAY	T0091	7.57	15	0.11	0.92	11.1	[a]	12	1mL	6	15.3	15.5	
ASSAY	T0092	7.57	15	0.11	0.92	10.6	[a]	12	1mL	6	14.6	14.8	ASSAY
ASSAY	T0093	7.57	15	0.11	0.92	10.7	[a]	12	1mL	6	14.7	15.0	Average Conc.= 14.6
ASSAY	T0095	7.57	15	0.11	0.92	10	[a]	11	1mL	6	13.8	14.0	Std. Dev.= 0.71
ASSAY	T0096	7.57	15	0.11	0.92	9.7	[a]	11	1mL	6	13.4	13.6	C.V.= 4.87%
ASSAY	T0097	7.57	15	0.11	0.92	10.3	[a]	11	1mL	6	14.2	14.4	
3M	VK 03504C	37.9	15	0.57	0.9	35.2	0	39	1.5 mL	29	14.9	15.0	
3M	VK 03569C	37.9	15	0.57	0.9	34.1	0	38	1.6 mL	28	14.4	14.5	
3M	VK 03572C	37.9	15	0.57	0.9	32.8	0	36	1.5 mL	27	13.8	14.0	3M
3M	VK 03697C	37.9	15	0.57	0.9	32.9	0	37	1.5 mL	27	13.9	14.0	Average Conc.= 14.1
3M	VK 03840C	37.9	15	0.57	0.9	31.7	0	35	1.5 mL	26	13.4	13.5	Std. Dev.= 0.59
3M	VK 04003C	37.9	15	0.57	0.9	31.7	0	35	1.5 mL	26	13.4	13.5	C.V.= 4.16%
3M	VK 03533C BLK	37.9	15	0.57	0.9	0	0	0	1.5 mL	0	0.0	0.0	

[a] There is only one section to these samples.
[b] Corrected for desorption volume differences.

Temperature= 19.9 degrees Celsius
Pressure= 752 mm Hg

Results for Methylene Chloride Passive Dosimeter Field Validation (Run # 9, STEL # 4, 12-14-94).

Active Samples

Pump ID	Sample ID	Pre- Cal (mL/min)	Post-Cal (mL/min)	Avg (mL/min)	Sample Time(min)	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Concentration (ppm)	
10374	9-MCT-A	99.84	98.37	99.11	15	1.49	1	618	0	618	2mL	119.7	
10375	9-MCT-B	99.23	96.9	98.07	15	1.47	1	460	0	460	2mL	90.0	
10376	9-MCT-C	102.7	100.5	101.60	15	1.52	1	658	0	658	2mL	124.3	MCT
10377	9-MCT-D	101.9	96.76	99.33	15	1.49	1	438	0	438	2mL	84.6	Average Conc.= 113.1
10378	9-MCT-E	102.1	99.65	100.88	15	1.51	1	775	0	775	2mL	147.4	Std. Dev.= 23.20
10379	9-MCT-F	101.8	100.5	101.15	15	1.52	1	592	0	592	2mL	112.3	C.V.= 20.52%
10380	9-MCT-BLANK	100.5	98.73	99.62	15	1.49	1	0	0	0	2mL	0.0	
10391	9-CMS-A	100.7	101.7	101.20	15	1.52	0.976	607	0	622	2mL	117.9	
10426	9-CMS-B	100.7	100.4	100.55	15	1.51	0.976	374	0	383	2mL	73.1	
10427	9-CMS-C	100.8	101.2	101.00	15	1.52	0.976	609	0	624	2mL	118.6	CMS
10428	9-CMS-D	99.02	97.88	98.46	15	1.48	0.976	467	0	478	2mL	93.3	Average Conc.= 104.4
10429	9-CMS-E	101.7	100.9	101.30	15	1.52	0.976	724	0	742	2mL	140.5	Std. Dev.= 25.46
10430	9-CMS-F	100.1	99.9	100.00	15	1.50	0.976	423	0	433	2mL	83.2	C.V.= 24.4%
10389	9-CMS-BLANK	99.15	96.85	98.00	15	1.47	0.976	0	0	0	2mL	0.0	

Passive Dosimeters

Sample Type	Sample ID	Sampling ate(mL/mi	Sampling Time	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Corrected Total [b]	Concentration (ppm)	T/P Corrected Conc. (ppm)	
SKC	9-001	14.5	15	0.2175	0.96	75.6	[a]	79	2mL	79	104.2	104.3	
SKC	9-002	14.5	15	0.2175	0.96	90.1	[a]	94	2mL	94	124.2	124.2	
SKC	9-003	14.5	15	0.2175	0.96	78.8	[a]	82	2mL	82	108.6	108.7	SKC
SKC	9-004	14.5	15	0.2175	0.96	72.4	[a]	75	2mL	75	99.8	99.8	Average Conc.= 116.3
SKC	9-005	14.5	15	0.2175	0.96	102.2	[a]	106	2mL	106	140.9	140.9	Std. Dev.= 15.22
SKC	9-006	14.5	15	0.2175	0.96	87.1	[a]	91	2mL	91	120.1	120.1	C.V.= 13.09%
SKC	9-BLANK	14.5	15	0.2175	0.96	0	[a]	0	2mL	0	0.0	0.0	
ASSAY	T0041(Blank)	7.57	15	0.11	0.92	0	[a]	0	1mL	0	0.0	0.0	
ASSAY	T0042	7.57	15	0.11	0.92	87.1	[a]	95	1mL	47	120.0	120.0	
ASSAY	T0044	7.57	15	0.11	0.92	73.9	[a]	80	1mL	40	101.8	101.8	ASSAY
ASSAY	T0045	7.57	15	0.11	0.92	72.8	[a]	79	1mL	40	100.3	100.3	Average Conc.= 106.8
ASSAY	T0046	7.57	15	0.11	0.92	87.6	[a]	95	1mL	48	120.7	120.7	Std. Dev.= 12.03
ASSAY	T0048	7.57	15	0.11	0.92	78.2	[a]	85	1mL	43	107.7	107.8	C.V.= 11.3%
ASSAY	T0050	7.57	15	0.11	0.92	65.2	[a]	71	1mL	35	89.8	89.9	
3M	VK 03588C	37.9	15	0.57	0.9	196	0	218	1.5 mL	163	82.7	82.7	
3M	VK 03630C	37.9	15	0.57	0.9	191	0	212	1.5 mL	159	80.6	80.6	
3M	VK 03839C	37.9	15	0.57	0.9	214	0	238	1.5 mL	178	90.3	90.3	3M
3M	VK 03956C	37.9	15	0.57	0.9	200	0	222	1.5 mL	167	84.4	84.4	Average Conc.= 85.9
3M	VK 04070C	37.9	15	0.57	0.9	184	0	204	1.5 mL	153	77.6	77.6	Std. Dev.= 8.09
3M	VK 04119C	37.9	15	0.57	0.9	237	0	263	1.5 mL	198	100.0	100.0	C.V.= 9.41%
3M	VK 03599C BLK	37.9	15	0.57	0.9	0	0	0	1.5 mL	0	0.0	0.0	

[a] There is only one section to these samples.
[b] Corrected for desorption volume differences.

Temperature= 21.8 degrees Celsius
Pressure= 748 mm Hg

3M 110666

Results for Methylene Chloride Passive Dosimeter Field Validation (Run # 10, STEL # 5, 1-10-95).

Active Samples

Pump ID	Sample ID	Pre- Cal (mL/min)	Post-Cal (mL/min)	Avg (mL/min)	Sample Time(min)	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Concentration (ppm)	
10374	10-MCT-A	102.2	102.9	102.55	15	1.54	1	496	0	496	2mL	92.8	
10375	10-MCT-B	100.9	99.37	100.14	15	1.50	1	504	0	504	2mL	96.6	
10376	10-MCT-C	99.21	100.4	99.81	15	1.50	1	493	0	493	2mL	94.8	MCT
10377	10-MCT-D	99.49	100.9	100.20	15	1.50	1	523	0	523	2mL	100.2	Average Conc.= 96.2
10378	10-MCT-E	100.4	100.6	100.50	15	1.51	1	487	0	487	2mL	93.0	Std. Dev.= 3.20
10379	10-MCT-F	100.4	100	100.20	15	1.50	1	520	0	520	2mL	99.6	C.V.= 3.32%
10380	10-MCT-BLANK	101.9	100.2	101.05	15	1.52	1	13.7	0	14	2mL	2.6	
10391	10-CMS-A	99.92	99.38	99.65	15	1.49	0.976	506	0	618	2mL	99.8	
10426	10-CMS-B	101.7	90.07	95.89	15	1.44	0.976	465	0	476	2mL	95.4	
10427	10-CMS-C	99.29	96.94	98.12	15	1.47	0.976	468	0	480	2mL	93.8	CMS
10428	10-CMS-D	97.19	95.41	96.30	15	1.44	0.976	513	0	526	2mL	104.7	Average Conc.= 99.4
10429	10-CMS-E	100.7	101.2	100.95	15	1.61	0.976	513	0	526	2mL	99.9	Std. Dev.= 4.23
10430	10-CMS-F	100.3	102.1	101.20	15	1.52	0.976	530	0	543	2mL	103.0	C.V.= 4.3%
10389	10-CMS-BLANK	100.4	101.2	100.80	15	1.51	0.976	13.2	0	14	2mL	2.6	

Passive Dosimeters

Sample Type	Sample ID	Sampling Rate(mL/min)	Sampling Time	Total Vol (L)	Desorption Efficiency	Analyzed amount (mcg/2mL) Front	Back	Total	Desorption Volume (mL)	Corrected Total [b]	Concentration (ppm)	T/P Corrected Conc. (ppm)	
SKC	10-001	14.6	15	0.2175	0.96	93.3	[a]	97	2mL	97	128.6	127.8	
SKC	10-002	14.5	15	0.2175	0.96	78.3	[a]	82	2mL	82	107.9	107.2	
SKC	10-003	14.5	15	0.2175	0.96	84.3	[a]	88	2mL	88	116.2	115.5	SKC
SKC	10-004	14.5	16	0.2175	0.96	82.6	[a]	86	2mL	86	113.9	113.1	Average Conc.= 113.9
SKC	10-005	14.5	15	0.2175	0.96	77.4	[a]	81	2mL	81	106.7	106.0	Std. Dev.= 7.78
SKC	10-006	14.5	15	0.2175	0.96	83.1	[a]	87	2mL	87	114.6	113.8	C.V.= 6.83%
SKC	10-BLANK	14.5	15	0.2175	0.96	0	[a]	0	2mL	0	0.0	0.0	
ASSAY	T0043(Blank)	7.57	15	0.11	0.92	0	[a]	0	1mL	0	0.0	0.0	
ASSAY	U1012	7.57	15	0.11	0.92	74.9	[a]	81	1mL	41	103.2	102.5	
ASSAY	U1013	7.57	15	0.11	0.92	80.8	[a]	88	1mL	44	111.3	110.6	ASSAY
ASSAY	U1014	7.57	15	0.11	0.92	84.8	[a]	92	1mL	46	116.8	116.1	Average Conc.= 108.0
ASSAY	U1017	7.57	15	0.11	0.92	77.9	[a]	85	1mL	42	107.3	106.6	Std. Dev.= 4.77
ASSAY	U1020	7.57	15	0.11	0.92	78.2	[a]	85	1mL	43	107.7	107.0	C.V.= 4.4%
ASSAY	U1038	7.57	15	0.11	0.92	76.7	[a]	83	1mL	42	105.7	106.0	
3M	VK 03767C	37.9	16	0.57	0.9	210	0	233	1.5 mL	176	88.6	88.6	
3M	VK 03884C	37.9	16	0.57	0.9	212	0	236	1.5 mL	177	89.6	89.5	
3M	VK 03905C	37.9	15	0.57	0.9	212	0	236	1.5 mL	177	89.5	89.5	3M
3M	VK 03936C	37.9	15	0.57	0.9	212	0	236	1.5 mL	177	89.5	89.5	Average Conc.= 87.6
3M	VK 03972C	37.9	15	0.57	0.9	219	0	243	1.5 mL	183	92.4	92.4	Std. Dev.= 5.83
3M	VK 03991C	37.9	15	0.57	0.9	180	0	200	1.5 mL	150	75.9	75.9	C.V.= 6.66%
3M	VK 03554C BLK	37.9	15	0.57	0.9	6.62	0	7	1.5 mL	6	2.8	2.8	

[a] There is only one section to these samples.
[b] Corrected for desorption volume differences.

Temperature= 23.2 degrees Celsius
Pressure= 748 mm Hg

3M 110667

FIELD VALIDATION OF PASSIVE DOSIMETERS FOR THE DETERMINATION OF EMPLOYEE EXPOSURES TO METHYLENE CHLORIDE ALONG WITH OTHER ORGANIC VAPORS IN HOSPITAL PRODUCTS PRODUCTION FACILITIES

Proposed Validation Study: March 15, 1995

Kem Charron and Mark Puskar
Corporate Industrial Hygiene Laboratory, Abbott Laboratories

Introduction:

To increase the ability of Abbott's industrial hygiene staff to collect data on employee exposures to multiple organic vapors in conjunction with Methylene Chloride (MeCl2), the Corporate Industrial Hygiene Laboratory (CIHL) has committed itself to performing a "peer-review-quality" field validation of passive dosimeters for long-term (PEL) exposures to multiple components. The goal of this validation project will be to determine if a passive dosimeter can replace our current active method (600 mg Charcoal tube), for the determination of employee exposures to multiple organic vapors of which MeCl2 is one of the components. The other organic solvents which may potentially be present are: acetone, chloroform, cyclohexanone, ethanol, ethyl acetate, Freon-113, heptane, methyl ethyl ketone, 2-propanol, toluene, 1,1,1-trichloroethane and trichloroethylene. Due to the complexity of this study, only area samples will be studied. No personal data will be collected.

To enhance the strength of this study, manufacturers of passive dosimeters are requested to take part in this investigation. However, this is strictly optional and the study will be conducted with or without the manufacturers' participation.

The proposed validation will include three types of passive dosimeters, each from a different manufacturer. The manufacturers/vendors include: Assay Technologies, 3M, and SKC. Each brand of monitor uses proprietary collection systems and a different methylene chloride extraction technique, however GC-FID analysis is similar to all the monitors. During the field validation exposures, air samples will be concurrently collected on 600 mg Charcoal tubes. Temperature, pressure, air velocity and humidity readings will be recorded at each sampling location.

Validation Study Design:

Abbott's Hospital Products Division (HPD), in Laurinburg, NC has been selected as the location to validate the methods because of two reasons:

(1) the first reason is its location. The HPD facility is located in North America. This will allow the field validation to be performed within the Continental United States.

(2) recent data suggest that there are multiple organic solvents present with MeCl2 concentrations over a wide range. This will allow the method to be tested over the full range of MeCl2 concentrations expected in other locations of the corporation.

Based on previous air monitoring results, 5 sampling locations in HPD's solvent sealing facility will be selected to test the full concentration range of MeCl2 with multiple organic solvent concentrations for PEL monitoring. The approximate concentrations to be studied are:

PEL: 8-hr TWA Samples

Location Number	Ideal Concentration in ppm MeCl
1	<10
2	10
3	25
4	50
5	>50

An exposure chamber has been built to expose an array of samples at each sampling location. Below is a list of the samples which will be collected at each of the 5 locations:

Samples to be Collected at Each Location

Number of Samples	Type	Frequency of Collection
6	Assay Technologies: MeCl Monitor	8-hr
6	3M: MeCl Monitor	8-hr
6	SKC: MeCl Monitor	8-hr
6	Charcoal Active Samples	8-hr
1	Temperature	randomly
1	Humidity	randomly
1	Pressure	randomly
1	Air Velocity	randomly

To accurately field validate MeCl monitors, two major problems must be overcome. The first problem is that a system must be developed where all monitors are turned on and off simultaneously. The second problem is that unique organic solvent concentrations may exist around different samples at the same location. If so, this must be understood, otherwise a false increased precision error would be added to all methods.

These two effects will be limited with the exposure chamber designed and built. This exposure chamber was developed and built for an EtO EL study which was previously performed. [1,2]. The chamber features a two dimensional array stand for dosimeter exposure mounted inside a Plexiglas chamber. The height of the dosimeters can be adjusted so each active exposure area is on the same horizontal plane. The Plexiglas cover can be removed once the chamber is in the sampling area, so all the dosimeters can be exposed at once. Once sampling is completed and the hood is placed back over the sampling array and sealed down (dual Teflon gaskets), the inside can be purged with organic solvent free compressed air to remove residual solvent. This residual solvent and excess purge air vent through the one way values mounted on the top of the chamber. This design should allow equal exposure of all the dosimeters for the same sampling time.

During each dosimeter exposure, six 600 mg Charcoal tubes will be sampled from six points circling the dosimeter array. Four of the sampling points are at each of the four corners of the dosimeter exposure horizontal plane. Point five is above the plane 4 inches and point 6 is below the plane 4 inches. These six charcoal tubes will be analyzed with the dosimeters and used to determine the actual concentration present and to determine if unique atmospheres may have existed at unique sampling location during the sample collection.

Collection Strategy:

The following collection strategy will be followed at each location studied.

1. The Purged/MeCl Free Chamber will be opened in an organic solvent free area (<0.1 ppm by GC-FID). Blanks will be opened and left in the organic solvent free area during the exposure to document that the area is free of organic solvents.

2. Monitors will be hung randomly across the two dimensional grid. The active sampling methods will be setup and connected to their pumps.

3. The chamber will be closed and MeCl-free air will be purged through the chamber during the chamber movement process from the clean area to the exposure area.

4. Once in the exposure area, the chamber will be opened and all the pumps will be started. Exposure time will be 480 minutes.

5. After exposure, the lid will be placed over the sampling grid and locked down. The purge air will be turned on and all sampling pumps will be turned off. The air flow rate will be sufficient to cause three complete air changes in the first 30 seconds.

6. The purge air will remain on until the chamber is successfully back in the organic solvent free area (<5 min.). The chamber will be opened and the samples will be removed.

7. All monitors will be Federal Expressed Over-night-air shipped to the CIHL.

8. All monitors will be stored in the CIHL according to manufacturer's instruction and analyzed within 2-week of collection.

Calibration of Equipment:

Gilian pumps will be used to collect the active samples. The Gilian pumps will be individually calibrated using a Gilibrator Primary Flow Calibrator.

Analysis of Samples:

All passive monitors will be extracted using the manufactures' instructions and will be analyzed using Hewlett Packard 5890 Series II GC-FID. Separation will be performed using a 100m PONA 0.2 mm ID column. Standards will be prepared in CS_2 and laboratory MeCl QA/QC samples will be analyzed with each set of samples. The MeCl QA/QC samples and the 600 mg Charcoal tube samples will be desorbed as outlined in CIHL's MeCl Air Monitoring Method.

Data Interpretation and Report Generation:

A full statistical analysis will be performed on the data generated from this study, and conclusions will be made regarding each of the methods. Depending on the results, Abbott may decide to publish this study as a peer-review article, as we did with the previous EtO Studies. [1-3]

Role of HPD Facility: Assist in identifying locations for field validation.

Role of the Manufacturer During the Validation Study:

1. Supply Abbott with 35 passive monitors along with all sampling/analysis instructions (5 sites x [6 samples + 1 blank] = 35). Advise Abbott's sampling staff on proper sampling, handling, preservation, and shipping procedures to assure that samples taken are not compromised.

2. Each manufacturer will be asked to comment on the study on three different occasions. This is strictly optional. By commenting or choosing not to comment, Abbott will not imply that the manufacturer agreed or disagreed with the study design, results or conclusions. These decisions will strictly be Abbott's. To expedite this study, comments must be received in writing within ten working days of receiving a request for comments. The first request for comment is upon receiving this document. Abbott is interested in receiving suggestions on enhancing and or adapting the proposed study design.

3. The second request for comments will be made after the raw data is collected and has been pooled. Each manufacturer, if interested, will be allowed to interpret all the raw data and submit suggested discussion topics and conclusions. The final request for comment will be made if Abbott decides to publish the study. An opportunity to comment on the manuscript will be given to each manufacturer prior to its submittal.

Listed below are the current contacts for this study:

Name	Company	Phone Number
Kem Charron	Abbott	708-938-6680
Martin Harper	SKC	412-941-1369
Gus Manning	Assay Technology	415-424-9945
Bob Weber	3M	612-737-4459

References:

1. Puskar, M.A., Szopinski, F.G., and Hecker, L.H., "Development and Validation of a Protocol for Field Validation of Passive Dosimeters for Ethylene Oxide Excursion Limit Monitoring" **Amer. Ind. Hyg. Assoc. J., 52(4):145-150 (1991).**

2. Szopinski, F.G., Puskar, M.A., and Hecker, L.H. "Field Validation of Three Passive Dosimeters for Excursion Limit Monitoring of Ethylene Oxide" **Amer. Ind. Hyg. Assoc. J., 52(4):151-157 (1991).**

3. Puskar, M.A. and Hecker, L.H., "Field Validation of Passive Dosimeters For the Determination of Employee Exposure to Ethylene Oxide in Hospital Product Sterilization Facilities," **Amer. Ind. Hyg. Assoc. J., 50(1): 30-36 (1989).**

Comments and/or Questions should be directed to:

Kem A. Charron
Industrial Hygiene Chemist
Abbott Laboratories, D-38A
1401 Sheridan Road
North Chicago, IL 60064
708-938-6680

3M Occupational Health and
Environmental Safety Division

3M Center
St. Paul, MN 55144-1000
612 733 1110

3M June 17, 1994

Mark Puskar
Abbott Laboratories, D-038A
Corporate Industrial Hygiene Lab
1401 Sheridan Rd.
North Chicago, IL 60064

Dear Mark:

We reviewed your proposed methylene chloride study and we would like to participate with our 3M 3520 Organic Vapor Monitor. However, it should be noted that our 3M 3520 Organic Vapor Monitor has limitations.

The monitor has an approximate maximum capacity of 3000 micrograms at high relative humidities (i.e., > 60%). The capacity will increase as relative humidity drops. Based on a capacity of 3000 micrograms at a high humidity, the maximum concentration measurements are as follows:

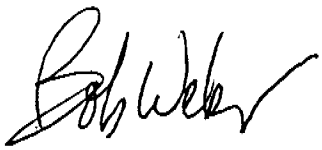
15 minutes:	1518 ppm
240 minutes:	120 ppm
480 minutes:	60 ppm

Based on this information, we recommend to our customers that sampling be limited to four hours when methylene chloride concentrations are unknown. However, if concentrations are expected to be at 50 ppm or below, the use of the 3520 monitor for eight hours is acceptable.

The validation study that Abbott outlined calls for a sampling site that is greater than 50 ppm methylene chloride. If an 8 hour sample was collected at this location, it is feasible that the capacity of the monitor may be exceeded. This sampling site pushes the limitation of the monitor. However, all of the other sampling sites, including the sampling times, fall within the limitations of the 3M 3520 monitor. We would like to participate in the study, however, we want to caution you that our 3M 3520 monitor cannot be used in all situations, just like most other sampling devices.

Please let me know when you would like the samples and other information. I look forward to working with you and Abbott. If you have any questions, please call me at 612-737-4459.

Regards,



Robert A. Weber, CIH
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bc: A.R. Johnston - 260-3B-09
D.J. Larsen - 260-3B-08
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G.H. Smith - 275-6W-01
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ABBOTT

June 15, 1992

Abbott Laboratories
North Chicago, Illinois 60064

Martin Harper	SKC
Gus Manning	Assay Technology
Donald Larsen	3M
Linda Smith	Gilian Environmental

cc:

Scott Fergon	Abbott Laboratories: CIHL
Larry Hecker	Abbott Laboratories: CIHT
Natalie Lisle	Abbott Laboratories: CAPD

FIELD VALIDATION OF PASSIVE DOSIMETERS FOR THE DETERMINATION OF EMPLOYEE EXPOSURES TO METHYLENE CHLORIDE IN PHARMACEUTICAL PRODUCTION FACILITIES

Enclosed for your review and comments is a copy of the proposed protocol for field validation of passive dosimeters for methylene chloride. We hope to begin the preliminary laboratory work (Tedlar bag evaluations) this month and will be ready to receive your Quality Control monitors by mid to late-July. If all goes well, we will begin the actual field work by late August.

If you have any questions or comments regarding the study please feel free to contact me.

Sincerely,

Mark A. Puskar

Mark A. Puskar, Ph.D.
Manager, Corporate Industrial Hygiene Laboratory
Abbott Laboratories D-038A
1401 Sheridan Road
North Chicago, IL 60064
(708) 937-4520
(708) 937-6293

FIELD VALIDATION OF PASSIVE DOSIMETERS FOR THE DETERMINATION OF EMPLOYEE EXPOSURES TO METHYLENE CHLORIDE IN PHARMACEUTICAL PRODUCTION FACILITIES

Proposed Validation Study: June 15, 1992

Mark Puskar and Scott Fergon
Corporate Industrial Hygiene Laboratory, Abbott Laboratories

Introduction:

To increase the ability of Abbott's industrial hygiene staff to collect data on employee exposures to methylene chloride (MeCl), the Corporate Industrial Hygiene Laboratory (CIHL) has committed itself to performing a "peer-review-quality" field validation of passive dosimeters, for both long-term (PEL) and short-term STEL exposures to methylene chloride. The goal of this validation project will be to determine if a passive dosimeter can replace our current active method (600 mg Charcoal tube), for the determination of employee exposures to MeCl. Due to the complexity of this study, only area samples will be studied. No personal data will be collected.

Due to the unfamiliarity of the CIHL with passive MeCl monitoring methods and to enhance the strength of this study, manufacturers of MeCl passive dosimeters are requested to take part in this investigation. However, this is strictly optional and the study will be conducted with or without the manufacturers' participation.

The proposed validation will include four types of passive dosimeters, each from a different manufacturer. The manufacturers/vendors include: Assay Technologies, 3M, SKC, and Gilian. Each brand of monitor uses proprietary collection systems and a different methylene chloride extraction technique, however GC-FID analysis is similar to all the monitors. During the field validation exposures, air samples will be concurrently collected into Tedlar bags and will be analyzed onsite with a GC-FID. Temperature, pressure, air velocity and humidity readings will be recorded at each sampling location.

Validation Study Design:

Abbott's Chemical Manufacturing Facility (CAPD), in North Chicago, IL has been selected as the location to validate the methods because of two reasons:

(1) the first reason is its location. CAPD is in the same location as the CIHL. This will allow the field validation to be performed near the labs location, reducing the need to ship equipment and lab personnel.

(2) recent data suggest that a wide range of MeCl levels currently exist in CAPD. This will allow the methods to be tested over the full range of MeCl concentrations expected in the corporation.

Using Tedlar air sampling bags and a Hewlett Packard Model 5890 Series II GC-FID with a 1-mL sampling loop, 10 sampling locations in CAPD's pharmaceutical manufacturing facility will be selected to test the full range of EtO concentrations for both PEL and STEL monitoring. The approximate concentrations to be studied are:

PEL: 8-hr TWA Samples

Location Number	Ideal Concentration in ppm MeCl
1	<10
2	10
3	25
4	50
5	>50

STEL: 15-min. TWA Samples

Location Number	Ideal Concentration in ppm MeCl
6	<25
7	50
8	125
9	300

10	>300	

An exposure chamber has been built to expose an array of samples at each sampling location. Below is a list of the samples which will be collected at each of the 10 locations:

Samples to be Collected at Each Location

Number of Samples	Type	Frequency of Collection
6	Assay Technologies: MeCl Monitor	8-hr and 15-min.
6	Gilian: MeCl Monitor	8-hr and 15-min.
6	3M: MeCl Monitor	8-hr and 15-min.
6	SKC: MeCl Monitor	8-hr and 15-min.
6	Tedlar Sampling Bags	8-hr and 15-min.
6	Charcoal Active Samples	8-hr and 15-min.
6	Additional Adsorbent Samples (SKC)	8-hr and 15-min.
1	Temperature	continuous
1	Humidity	continuous
1	Pressure	continuous
1	Air Velocity	continuous

To accurately field validate MeCl monitors, two major problems must be overcome. The first problem is that a system must be developed where all monitors are turned on and off simultaneously. The second problem is that unique MeCl concentrations may exist around different samples at the same location. If so, this must be understood, otherwise a false increased precision error would be added to all methods.

These two effects will be limited with the exposure chamber designed and built. This exposure chamber was developed and built for an EtO EL study which was previously performed. [1,2] Pictures of the chamber are provided in the enclosed manuscripts. The chamber features a two dimensional array stand for dosimeter exposure mounted inside a Plexiglas chamber. The height of the dosimeters can be adjusted so each active exposure area is on the same horizontal plane. The Plexiglas cover can be removed once the chamber is in the sampling area, so all the dosimeters can be exposed at once. Once sampling is completed and the hood is placed back over the sampling array and sealed down (dual Teflon gaskets), the inside can be purged with MeCl free compressed air to remove residual MeCl.

This residual MeCl and excess purge air vent through the one way values mounted on the top of the chamber. This design should allow equal exposure of all the dosimeters for the same sampling time.

During each dosimeter exposure, six Tedlar air sampling bags will be filled from six points circling the dosimeter array. Four of the sampling points are at each of the four corners of the dosimeter exposure horizontal plane. Point five is above the plane 4 inches and point 6 is below the plane 4 inches. These six bags will be analyzed immediately after sample collection (on site in triplicate) to determine the actual concentration present and to determine if unique atmospheres may have existed at unique sampling location during the sample collection.

Two active sampling methods will also be collected at each location. The first active method will be 600 mg activated charcoal tubes (Abbott's current method for monitoring MeCl). The second method will be an adsorbent SKC recommends for monitoring MeCl.

All preliminary studies necessary to document that the Tedlar air sampling bag method will be appropriate to estimate "actual-concentration-present" during the field validation will be performed following the protocol described in reference 1. These studies will include: validation of MeCl stability in Tedlar bags, validation of sampling process, and external verification of primary MeCl diffusion vial standard.

Collection Strategy:

The following collection strategy will be followed at each location studied.

1. The Purged/MeCl Free Chamber will be opened in an MeCl Free Area (<0.1 ppm by GC-FID). Blanks will be opened and left in the MeCl free area during the exposure to document that the area is MeCl free.

2. Monitors will be hung randomly across the two dimensional grid. The active sampling methods will be setup and connected to their pumps.

3. The chamber will be closed and MeCl-free air will be purged through the chamber during the chamber movement process from the clean area to the exposure area.

4. Once in the exposure area, the chamber will be opened and all the pumps will be started, including the six Tedlar bag pumps. Each Tedlar bag pump will draw air into a MeCl-free Tedlar bag. Exposure time will be either 15 or 480 minutes.

5. After exposure, the lid will be placed over the sampling grid and locked down. The purge air will be turned on and all sampling pumps will be turned off. The air flow rate will be sufficient to cause three complete air changes in the first 30 seconds.

6. The purge air will remain on until the chamber is successfully back in the MeCl Free Area (<5 min.). The chamber will be opened and the samples will be removed.

7. The six Tedlar bags will be analyzed immediately on site by GC-FID. After use, each Tedlar bag will be purged with MeCl free air. GC-FID verification will be performed prior to reuse.

8. All monitors will be Federal Expressed Over-night-air shipped to a secondary Abbott Location and then returned shipped to the CIHL to document any possible shipping effects.

9. All monitors will be stored in the CIHL according to manufacturer's instruction and analyzed within 1-week of collection.

Calibration of Equipment:

Gilian pumps will be used to collect the Tedlar Bag samples (0.02 lpm or 0.5 lpm). The GC-FID, used to analyze the Tedlar Bags, will be calibrated prior to and after each days sampling using a Dynacalibrator diffusion vial system. A middle standard will be analyzed every 10-15 injections. The active samples will be collected using Low-Flow Gilian pumps.

Analysis of Samples:

All passive monitors will be extracted using the manufactures' instructions and will be analyzed using Hewlett Packard 5890 Series II GC-FID. Separation will be performed using a 100m PONA 0.2 mm ID column. Standards will be prepared in CS_2 and laboratory MeCl QA/QC samples will be analyzed with each set of samples.

Data Interpretation and Report Generation:

A full statistical analysis will be performed on the data generated from this study, and conclusions will be made regarding each of the methods. Depending on the

results, Abbott may decide to publish this study as a peer-review article, as we did with the previous EtO Studies. [1-3]

Role of the Manufacturer During the Validation Study:

1. Supply Abbott with 70 passive monitors along with all sampling/analysis instructions (10 sites x [6 samples + 1 blanks] = 70). Advise Abbott's sampling staff on proper sampling, handling, preservation, and shipping procedures to assure that sample taken are not compromised.

2. Each manufacturer will be asked to comment on the study on three different occasions. This is strictly optional. By commenting or choosing not to comment, Abbott will not imply that the manufacturer agreed or disagreed with the study design, results or conclusions. These decisions will strictly be Abbott's. To expedite this study, comments must be received in writing within ten working days of receiving a request for comments. The first request for comment is upon receiving this document. Abbott is interested in receiving suggestions on enhancing and or adapting the proposed study design.

3. The second request for comments will be made after the raw data is collected and has been pooled. Each manufacturer, if interested, will be allowed to interpret all the raw data and submit suggested discussion topics and conclusions. The final request for comment will be made if Abbott decides to publish the study. An opportunity to comment on the manuscript will be given to each manufacturer prior to its submittal.

Listed below are the current contacts for this study:

Name	Company	Phone Number
Mark Puskar	Abbott	708-937-4520
Martin Harper	SKC	412-941-1369
Gus Manning	Assay Technology	415-424-9945
Donald Larsen	3M	612-737-4103
Linda Smith	Gilian Environmental	804-431-2260

References;

1. Puskar, M.A., Szopinski, F.G., and Hecker, L.H., "Development and Validation of a Protocol for Field Validation of Passive Dosimeters for Ethylene Oxide Excursion Limit Monitoring" **Amer. Ind. Hyg. Assoc. J., 52(4):145-150 (1991).**

2. Szopinski, F.G., Puskar, M.A., and Hecker, L.H. "Field Validation of Three Passive Dosimeters for Excursion Limit Monitoring of Ethylene Oxide" **Amer. Ind. Hyg. Assoc. J., 52(4):151-157 (1991).**

3. Puskar, M.A. and Hecker, L.H., "Field Validation of Passive Dosimeters For the Determination of Employee Exposure to Ethylene Oxide in Hospital Product Sterlization Facilities," **Amer. Ind. Hyg. Assoc. J., 50(1): 30-36 (1989).**

Comments and/or Questions should be directed to:

Mark A. Puskar, Ph.D.
Manager, Corporate Industrial Hygiene Laboratory
Abbott Laboratories, D-38A
1401 Sheridan Road
North Chicago, IL 60064
708-937-4520

June 7, 1994

Don
We need to
talk
about this
BB

Martin Harper SKC
Gus Manning Assay Technology
Bob Weber 3M

cc:

Mark Puskar Abbott Laboratories: CIHL
Elisabel Puskar Abbott Laboratories: CAPD
Jim Murphy Abbott Laboratories: CHS

FIELD VALIDATION OF PASSIVE DOSIMETERS FOR THE DETERMINATION OF EMPLOYEE EXPOSURES TO METHYLENE CHLORIDE IN PHARMACEUTICAL PRODUCTION FACILITIES

Enclosed for your review is an updated protocol for the field validation of passive dosimeters for methylene chloride. This study was first proposed in 1992 and is now ready to be performed. The Corporate Industrial Hygiene Lab was supplied with methylene chloride spiked badges in 1992 which were analyzed to show that the Lab was capable of analyzing the dosimeters accurately. The Lab was successful in analyzing these spikes, however, since 1992 there have been some personnel changes. We feel that we are still capable of analyzing the samples accurately but are willing to analyze more blind spikes if you feel that it would be benificial.

The proposed start date for the field validation is July 15, 1994. We look forward to your participation in this study. If you have any questions or comments pleases feel free to contact Mark Puskar or myself.

Sincerely,

Kem A. Charron

Kem A. Charron
Industrial Hygiene Chemist
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FIELD VALIDATION OF PASSIVE DOSIMETERS FOR THE DETERMINATION OF EMPLOYEE EXPOSURES TO METHYLENE CHLORIDE IN PHARMACEUTICAL PRODUCTION FACILITIES

Proposed Validation Study: July 15, 1994

Mark Puskar and Kem Charron
Corporate Industrial Hygiene Laboratory, Abbott Laboratories

Introduction:

To increase the ability of Abbott's industrial hygiene staff to collect data on employee exposures to methylene chloride (MeCl), the Corporate Industrial Hygiene Laboratory (CIHL) has committed itself to performing a "peer-review-quality" field validation of passive dosimeters, for both long-term (PEL) and short-term STEL exposures to methylene chloride. The goal of this validation project will be to determine if a passive dosimeter can replace our current active method (600 mg Charcoal tube), for the determination of employee exposures to MeCl. Due to the complexity of this study, only area samples will be studied. No personal data will be collected.

Due to the unfamiliarity of the CIHL with passive MeCl monitoring methods and to enhance the strength of this study, manufacturers of MeCl passive dosimeters are requested to take part in this investigation. However, this is strictly optional and the study will be conducted with or without the manufacturers' participation.

The proposed validation will include three types of passive dosimeters, each from a different manufacturer. The manufacturers/vendors include: Assay Technologies, 3M, and SKC. Each brand of monitor uses proprietary collection systems and a different methylene chloride extraction technique, however GC-FID analysis is similar to all the monitors. During the field validation exposures, air samples will be concurrently collected on 600 mg Charcoal tubes. Temperature, pressure, air velocity and humidity readings will be recorded at each sampling location.

Validation Study Design:

Abbott's Chemical Manufacturing Facility (CAPD), in North Chicago, IL has been selected as the location to validate the methods because of two reasons:

(1) the first reason is its location. CAPD is in the same location as the CIHL. This will allow the field validation to be performed near the labs location, reducing the need to ship equipment and lab personnel.

(2) recent data suggest that a wide range of MeCl levels currently exist in CAPD. This will allow the methods to be tested over the full range of MeCl concentrations expected in the corporation.

Based on previous air monitoring results, 10 sampling locations in CAPD's pharmaceutical manufacturing facility will be selected to test the full range of MeCl concentrations for both PEL and STEL monitoring. The approximate concentrations to be studied are:

PEL: 8-hr TWA Samples

Location Number	Ideal Concentration in ppm MeCl
1	<10
2	10
3	25
4	50
5	>50

STEL: 15-min. TWA Samples

Location Number	Ideal Concentration in ppm MeCl
6	<25
7	50
8	125
9	300
10	>300

An exposure chamber has been built to expose an array of samples at each sampling location. Below is a list of the samples which will be collected at each of the 10 locations:

Samples to be Collected at Each Location

Number of Samples	Type	Frequency of Collection
6	Assay Technologies: MeCl Monitor	8-hr and 15-min.
6	3M: MeCl Monitor	8-hr and 15-min.
6	SKC: MeCl Monitor	8-hr and 15-min.
6	Charcoal Active Samples	8-hr and 15-min.
6	Additional Adsorbent Samples (SKC)	8-hr and 15-min.
1	Temperature	continuous
1	Humidity	continuous
1	Pressure	continuous
1	Air Velocity	continuous

To accurately field validate MeCl monitors, two major problems must be overcome. The first problem is that a system must be developed where all monitors are turned on and off simultaneously. The second problem is that unique MeCl concentrations may exist around different samples at the same location. If so, this must be understood, otherwise a false increased precision error would be added to all methods.

These two effects will be limited with the exposure chamber designed and built. This exposure chamber was developed and built for an EtO EL study which was previously performed. [1,2] The chamber features a two dimensional array stand for dosimeter exposure mounted inside a Plexiglas chamber. The height of the dosimeters can be adjusted so each active exposure area is on the same horizontal plane. The Plexiglas cover can be removed once the chamber is in the sampling area, so all the dosimeters can be exposed at once. Once sampling is completed and the hood is placed back over the sampling array and sealed down (dual Teflon gaskets), the inside can be purged with MeCl free compressed air to remove residual MeCl. This residual MeCl and excess purge air vent through the one way values mounted on the top of the chamber. This design should allow equal exposure of all the dosimeters for the same sampling time.

During each dosimeter exposure, six 600 mg Charcoal tubes will be sampled from six points circling the dosimeter array. Four of the sampling points are at each of the four corners of the dosimeter exposure horizontal plane. Point five is above the plane

4 inches and point 6 is below the plane 4 inches. These six charcoal tubes will be analyzed with the dosimeters and used to determine the actual concentration present and to determine if unique atmospheres may have existed at unique sampling location during the sample collection.

Another active sampling method will also be used to monitor the MeCl concentration at each location. This method will be an adsorbent SKC recommends for monitoring MeCl.

Collection Strategy:

The following collection strategy will be followed at each location studied.

1. The Purged/MeCl Free Chamber will be opened in an MeCl Free Area (<0.1 ppm by GC-FID). Blanks will be opened and left in the MeCl free area during the exposure to document that the area is MeCl free.

2. Monitors will be hung randomly across the two dimensional grid. The active sampling methods will be setup and connected to their pumps.

3. The chamber will be closed and MeCl-free air will be purged through the chamber during the chamber movement process from the clean area to the exposure area.

4. Once in the exposure area, the chamber will be opened and all the pumps will be started. Exposure time will be either 15 or 480 minutes.

5. After exposure, the lid will be placed over the sampling grid and locked down. The purge air will be turned on and all sampling pumps will be turned off. The air flow rate will be sufficient to cause three complete air changes in the first 30 seconds.

6. The purge air will remain on until the chamber is successfully back in the MeCl Free Area (<5 min.). The chamber will be opened and the samples will be removed.

7. All monitors will be Federal Expressed Over-night-air shipped to a secondary Abbott Location and then returned shipped to the CIHL to document any possible shipping effects.

8. All monitors will be stored in the CIHL according to manufacturer's instruction and analyzed within 1-week of collection.

Calibration of Equipment:

Gilian pumps will be used to collect the active samples. The Gilian pumps will be individually calibrated using a Gilibrator Primary Flow Calibrator.

Analysis of Samples:

All passive monitors will be extracted using the manufactures' instructions and will be analyzed using Hewlett Packard 5890 Series II GC-FID. Separation will be performed using a 100m PONA 0.2 mm ID column. Standards will be prepared in CS_2 and laboratory MeCl QA/QC samples will be analyzed with each set of samples. The MeCl QA/QC samples and the 600 mg Charcoal tube samples will be desorbed as outlined in CIHL's MeCl Air Monitoring Method. The samples collected using the SKC adsorbent will be desorbed using the manufactures' instructions.

Data Interpretation and Report Generation:

A full statistical analysis will be performed on the data generated from this study, and conclusions will be made regarding each of the methods. Depending on the results, Abbott may decide to publish this study as a peer-review article, as we did with the previous EtO Studies. [1-3]

Role of the Manufacturer During the Validation Study:

1. Supply Abbott with 70 passive monitors along with all sampling/analysis instructions (10 sites x [6 samples + 1 blank] = 70). Advise Abbott's sampling staff on proper sampling, handling, preservation, and shipping procedures to assure that samples taken are not compromised.

2. Each manufacturer will be asked to comment on the study on three different occasions. This is strictly optional. By commenting or choosing not to comment, Abbott will not imply that the manufacturer agreed or disagreed with the study design, results or conclusions. These decisions will strictly be Abbott's. To expedite this study, comments must be received in writing within ten working days of receiving a request for comments. The first request for comment is upon receiving this document. Abbott is interested in receiving suggestions on enhancing and or adapting the proposed study design.

3. The second request for comments will be made after the raw data is collected and has been pooled. Each manufacturer, if interested, will be allowed to interpret all the raw data and submit suggested discussion topics and conclusions. The final request for comment will be made if Abbott decides to publish the study. An

opportunity to comment on the manuscript will be given to each manufacturer prior to its submittal.

Listed below are the current contacts for this study:

Name	Company	Phone Number
Kem Charron	Abbott	708-938-6680
Martin Harper	SKC	412-941-1369
Gus Manning	Assay Technology	415-424-9945
Bob Weber	3M	612-737-4459

References:

1. Puskar, M.A., Szopinski, F.G., and Hecker, L.H., "Development and Validation of a Protocol for Field Validation of Passive Dosimeters for Ethylene Oxide Excursion Limit Monitoring" **Amer. Ind. Hyg. Assoc. J., 52(4):145-150 (1991).**

2. Szopinski, F.G., Puskar, M.A., and Hecker, L.H. "Field Validation of Three Passive Dosimeters for Excursion Limit Monitoring of Ethylene Oxide" **Amer. Ind. Hyg. Assoc. J., 52(4):151-157 (1991).**

3. Puskar, M.A. and Hecker, L.H., "Field Validation of Passive Dosimeters For the Determination of Employee Exposure to Ethylene Oxide in Hospital Product Sterilization Facilities," **Amer. Ind. Hyg. Assoc. J., 50(1): 30-36 (1989).**

Comments and/or Questions should be directed to:

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Long term sampling with diffusion monitors

By Donald J. Larsen and R bert A. Weber

Donald Larsen and Robert Weber are a Certified Industrial Hygienists with 3M Occupational Health and Environmental Safety Division.

Introduction

Historically, diffusion monitors have been used to monitor the work environment for full work shifts of eight hours. Lab and field evaluations by 3M and others have been performed over the last 20 years to validate diffusion monitors for eight-hour and short term exposure limit (STEL) sampling. Recent concern with indoor air quality, environmental emissions and hazardous waste disposal gives rise to situations where monitoring for extended periods is desirable. Also, since concentrations in indoor air quality investigations may be very low, long sampling times may be necessary to accumulate enough mass for analysis.

In long term diffusion sampling, the factor we were most interested in measuring was reverse diffusion. Reverse diffusion is the loss of previously adsorbed analyte during the sampling period. When this occurs, the sampling rate will be lower than predicted. Reverse diffusion effects can be studied by using a monitor that has a backup layer of sorbent and exposing the monitor to contamination levels that would not exceed the expected capacity of the primary layer. If the primary section on the monitor is not overloaded, any adsorbed material found on the backup section is due to reverse diffusion during sampling.

In this report, we will outline results of five laboratory experiments conducted with the following compounds:

- toluene
- 1,1,1-tricholoroethane
- acetone
- methyl ethyl ketone (MEK)
- methylene chloride.

The compounds selected enabled us to test several classes of compounds that have a range of boiling points and a range of affinities for activated carbon.

In each of the five lab studies, the mass of the collected analyte was measured and compared to the mass expected. The mass expected is derived from published sampling rates. A significant difference between the contaminant mass found and the mass expected would indicate contaminant loss and reverse diffusion.

Experimental design

To evaluate long term sampling performance of the 3M 3520 Organic Vapor Monitor, known air concentrations of analytes were generated in a laboratory generator/dilution system. The challenge concentration was also monitored by a portable infrared analyzer. A relative humidity of 30% and a temperature of 23°C was maintained within the system. The challenge concentration was passed through a Plexiglas chamber (5" x 5" x 21") containing the monitors. A challenge air flow of 90 Lpm created a face velocity of 19 feet per minute (fpm).

Experiment 1

Twelve monitors were exposed to 2.3 ppm of toluene. After 2.75 days, six of the monitors were removed and exposed to clean air for one, two or three days. The average amount found on the monitors given clean air exposure was the same as that found on the monitors exposed to toluene alone. In addition, no contaminant was found on the monitor backup sections.

Conclusion: If exposure occurred in the sampling period, followed by minimal or no exposure, no loss of contaminant occurred. These results indicate that reverse diffusion did not occur using 3M 3520 Organic Vapor Monitors under these conditions.

Experiment 2

Six monitors were exposed to 0.45 ppm of 1,1,1-trichloroethane. After four days, two monitors were removed and two new monitors were started. Sampling continued for another four days. The two groups of monitors exposed for four days showed no contaminant on their backup sections. Less than 1% of the total mass collected was found on the backup sections of the monitors exposed for eight days. The average amount of contaminant found was 0.83 mg compared to the amount expected of 0.86 mg.

Conclusion: This experiment indicates that the 3M 3520 Organic Vapor Monitor can be used for 1,1,1-trichloroethane monitoring at low concentrations for extended periods of time.

Experiment 3

Six monitors were exposed to 2.86 ppm of acetone for five days. Based on the published sampling rate, the contaminant amount expected was 1.97 mg acetone. The mean acetone level was 1.77 mg with a standard deviation of .063 and a coefficient variation of 3.55. This translates to an accuracy of ±17%. We found 15% of the total mass collected on the backup section.

Conclusion: This experiment indicates that the 3M 3520 Organic Vapor Monitor can be used to monitor acetone for extended periods of time.

Experiment 4

Twelve monitors were exposed to a mixture of 0.17 ppm toluene and 0.03 ppm of methyl ethyl ketone (MEK). Six monitors were removed after two weeks, three more after three weeks and the last three after four weeks of exposure. The contaminant amounts found were very close to the amounts expected (see Table 1). No toluene or MEK was found on the monitor backup sections. Figure 1 shows that the uptake rate was linear throughout the 28-day experiment.

Conclusion: This experiment demonstrates that the 3M 3520 Organic Vapor Monitor works accurately for long sampling periods.

Table 1
Exposure of 3M 3520 Organic Vapor Monitors to a mixture of 0.17 ppm t luene and 0.03 ppm MEK for 28 days

Toluene

Hours	Amount Expected (μg)	Amount Found (μg)
365	438	438±6.0%
500	618	615±4.7%
673	827	815±3.6%

MEK

Hours	Amount Expected (μg)	Amount Found (μg)
365	64	68±6.9%
500	93	100±3.9%
673	125	130±4.3%

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Experiment 5

Twenty-one monitors were involved in this experiment; some were exposed continuously and others intermittently to methylene chloride at 1.9 ppm for one to five days. Data from 15 monitors that were exposed continuously indicates the uptake rates remained linear throughout the exposure period. The remaining six monitors were exposed on a "day on/day off" basis to 1.9 ppm methylene chloride alternating with 0 ppm methylene chloride. The intermittently exposed monitors collected 95% of the amount on the monitors exposed continuously.

Conclusion: The 3M 3520 Organic Vapor Monitor works accurately for long sampling periods as well as intermittent exposure.

Conclusions

These experiments demonstrate that the 3M 3520 Organic Vapor Monitor can be used for extended sampling periods of approximately one week to one month with accurate results. When monitoring volatile compounds like acetone or methylene chloride, it is critical that a monitor with a backup section be used to achieve accepted industry standards for accuracy.

We can generalize our observations by recommending the use of a monitor with backup section for those compounds with boiling points below 60°C and recommending the use of a monitor without a backup section for those compounds with boiling points above 90°C. For those compounds with boiling points between 60°C and 90°C, a monitor with backup would provide higher accuracy with less risk of loss.

For more information on long term sampling, please call the 3M OH&ESD Technical Service Hotline at 1-800-243-4630.

Further Reading

Epstein, Paul S., et al: Experiences Using Passive Monitors to Measure Volatile Organic Compounds During Indoor and Ambient Air Quality Surveys, American Industrial Hygiene Conference, 1990.

Cohen, Martin A. et al: The Validation of a Passive Sampler for Indoor and Outdoor Concentrations of Volatile Organic Compounds, J. Air Waste Manage. 40:993(1990).

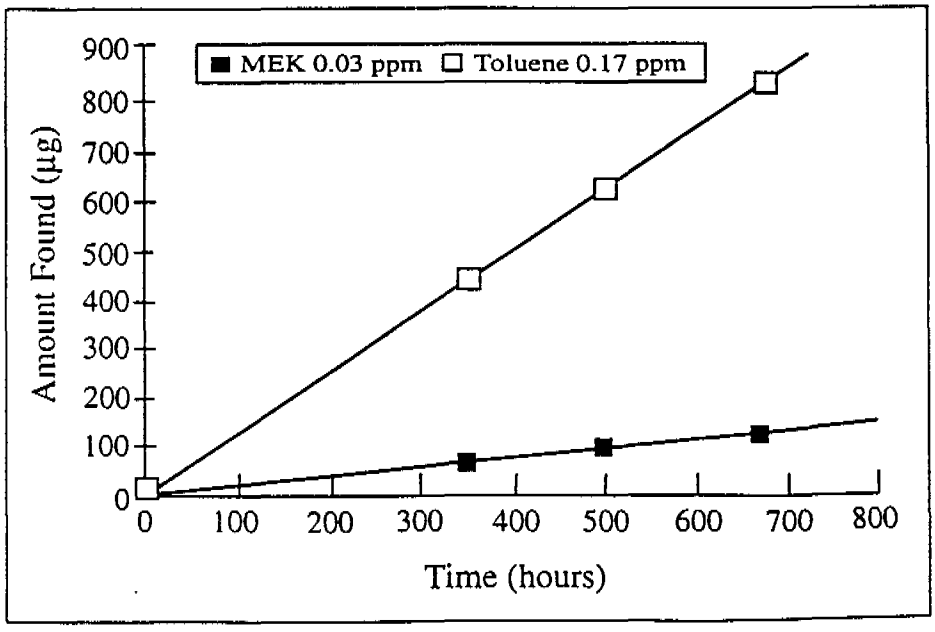

Figure 1. Linear uptake rates of MEK and toluene over 28 days demonstrate the long term sampling abilityy of the 3M 3520 Organic Vapor Monitor.

Internal Correspondence

3M

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From: R.A. Weber (7-4459) - OH&ESD - 260-3B-09

Subject: **MONITOR ARTICLE ON LONG TERM SAMPLING**

Date: September 13, 1994

Don Larsen and I have been working on developing technical information that can support our diffusion monitors. If you have time, I would like you to review and comment on the enclosed article by September 26, 1994. At this time, the information will be sent out to customers on request, however, we are considering publishing if it is worthy. When you review, please do it with a critical eye.

Thanks,

RAW:llj/145
Attachment

Long Term Sampling With Diffusion Monitors

Donald J. Larsen and Robert A. Weber
OH&ESD, 3M Company

INTRODUCTION

Historically diffusion monitors have been used for monitoring the working environment for full work shifts of 8 hours. Lab and field evaluations by 3M and others have been performed over the last 20 years to validate their use for 8 hour and STEL sampling.. Recent concern with indoor air quality, environmental emissions and hazardous waste disposal gives rise to situations where monitoring for extended periods is desirable. For indoor air quality investigations the concentrations may be very low, therefore long sampling times may be necessary to accumulate enough mass for analysis.

Validation of a diffusion monitor must address the following factors - whether the sampling period is 8 hours , 15 minutes or several weeks: recovery, analytical sensitivity, capacity/reverse diffusion, linear uptake rate, orientation, temperature, face velocity, interference and storage. Validation of active sampling tubes like charcoal tubes must address these issues also.

Reverse diffusion is the loss of previously adsorbed analyte during the sampling period. When this occurs with diffusion monitors the sampling rate will appear lower than predicted. Reverse diffusion effects can be studied by using a monitor that has a backup layer of sorbent and exposing the monitor to concentration levels that would not exceed the expected capacity of the primary layer. If the primary section on the monitor is not overloaded, any adsorbed material found on the backup section is due to reverse diffusion during sampling.

In this study we evaluated the long term sampling performance of the 3M 3520 Organic Vapor Monitor. This report outlines results of five labortory experiments conducted with toluene, 1,1,1-trichloroethane, acetone, methyl ethyl ketone (MEK), and methylene chloride and a field test that evaluated the performance of the organic vapor monitors during exposure to a mixture of n-butanol and isopropanol.

The compounds selected enabled us to test several classes of compounds that have a range of boiling points and a range of affinity for activated carbon.

EXPERIMENTAL DESIGN

To evaluate the performance of the monitors the known air concentrations of analytes were generated in a laboratory generator/dilution system. The challenge concentration was also monitored by a portable infrared analyzer. A relative humidity of 30% and a temperature of 23 °C. was maintained inside the system. The challenge concentration was passed through a Plexiglas chamber (5" x 5" x 21") containing the monitors. A challenge air flow of 90 Lpm created a face velocity of 19 feet per minute (fpm).

In each of the five lab studies, the mass of the collected analyte was measured and compared to the mass expected. The mass expected is derived from our published sampling rates. A significant difference between the contaminant mass found and the mass expected would indicate contaminant loss and reverse diffusion.

LABORATORY RESULTS

Experiment 1

Twelve monitors were exposed to 2.3 ppm of toluene. After 2.75 days, six of the monitors were removed and analyzed. The remaining six monitors were exposed to 0 ppm toluene for 1, 2 or 3 days and analyzed. The average amount found on the monitors given additional exposure was the statistically the same as that of the monitors exposed to toluene alone (table 1). Based on a sampling rate of 31.4 cc/min. for toluene the predicted concentration on the monitors was 1.09 ppm whereas the average of the twelve monitors was 1.09 ppm +/- 0.064. These results indicate that reverse diffusion did not occur using the 3M 3520 Monitors under these conditions.

TABLE 1

EXPOSURE TO 2.33 PPM TOLUENE FOR 2 3/4 DAYS
PLUS 1, 2, OR 3 DAYS AT 0 PPM

Set	Exposure days at 2.75 ppm toluene	Exposure days at 0 ppm toluene	n	Average	Standard deviation
1	2.75	0	6	1.122	0.03
2	2.75	1	2	1.055	0.122
3	2.75	2	2	1.062	0.102
4	2.75	3	2	1.084	0.067

Experiment 2

Six monitors were initially placed in the chamber and exposed to 0.45 ppm of 1,1,1 trichlororethane. After 4 days, 2 were removed and 2 new monitors were started. Sampling continued for another four days. The two 4 day exposures showed nothing on the back-up section. Less than 1% of the total mass collected was found on the back-up of the monitors exposed for 8 days. The average amount found based on a sampling rate of 30.9 cc/min. was 0.83 mg compared to the amount expected which was 0.86 mg (table 2). This experiment indicates that the 3M 3520 can be used for 1,1,1-trichloroethane at low concentrations for extended periods of time.

TABLE 2

EXPOSURE TO 0.45 PPM 1,1,1-TRICHLOROETHANE FOR 8 DAYS

Exposure	mg Expected	mg Found A	mg Found B	mg Total
First 4 Days	0.45	0.394	0.000	0.394
		0.445	0.000	0.445
Last 4 Days	0.41	0.393	0.000	0.393
		0.384	0.000	0.384
All 8 Days	0.86	0.890	0.005	0.901
		0.842	0.005	0.853
		0.772	0.004	0.781
		0.817	0.005	0.828
			Average 8 day exposure	0.830+/-0.044 (+/-5.3%)

Experiment 3

Six monitors were exposed to 2.86 ppm of acetone for 5 days. Based on the published sampling rate of 40.1cc/min. the amount expected over a five day period was 1.97 mg acetone. The mean acetone level was 1.77 mg with a standard deviation of .063 and a coefficient of variation of 3.55. This translates to an accuracy of 17.4%. For acetone, we found 15% of the total mass collected on the backup section (see table 3). If a single stage monitor had been used the amount on the back section would have been lost and this would have resulted in an accuracy of 40.9%.

TABLE 3

EXPOSURE TO 2.86 PPM ACETONE FOR 5 DAYS

ID	mg A	mg B	mg Total
1	1.343	0.202	1.788
2	1.288	0.222	1.776
3	1.287	0.203	1.765
4	1.307	0.199	1.744
5	1.411	0.209	1.871
6	1.270	0.189	1.685

average mg:1.767
standard deviation: 0.063
coefficient variation: 3.55%
amount (mg) expected : 1.97

Experiment 4

Twelve monitors were exposed to a mixture of 0.17 PPM toluene and 0.03 PPM of methyl ethyl ketone. Six monitors were removed after 2 weeks, three more after 3 weeks and the last three after 4 weeks of exposure. The amount found was very close to the amount expected. (table 4). No toluene or MEK was found on the backup sections showing that reverse diffusion did not occur even after this extended sampling time. Figure 1 shows that the uptake rate was linear throughout the 28 day experiment. This experiment demonstrates that the 3M 3520 organic vapor monitor works accurately for long sampling periods.

TABLE 4

28 DAY EXPOSURE TO MIXTURE OF 0.17 PPM TOLUENE AND 0.03 PPM MEK

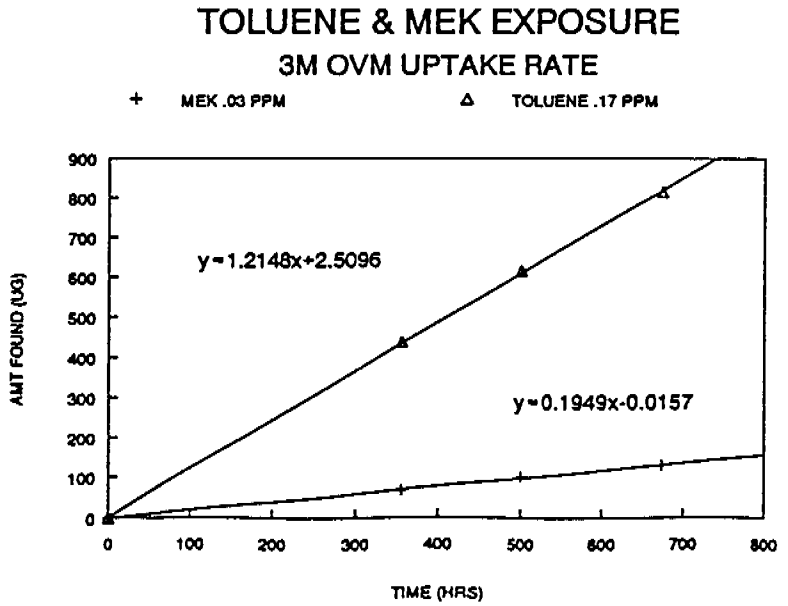
TOLUENE

HOURS	AMT EXPECTED UG	AMT. FOUND UG
356.3	438	438+/-6.0%
500.2	618	615+/-4.7%
673	827	815+/-3.6%

MEK

HOURS	AMT EXPECTED UG	AMT FOUND UG
356.3	64	68 +/-6.9%
500.2	93	100 +/-3.9%
673	125	130 +/-4.3%

FIGURE 1



Experiment 5

Twenty-one monitors were exposed continuously and intermittently to methylene chloride at 1.9 ppm for 1 to 5 days. Three monitors were removed each day and analyzed. Based on the 15 monitors exposed continuously over the five days, the uptake rate remained linear throughout this exposure. Analysis of the set indicated a coefficient of variation 5.3%, a bias of -3.2%, this translates to an accuracy of 13.8%.

The remaining six monitors were exposed "day on day off" to the methylene chloride, for a total of 0 ppm methylene chloride for 48 hours and 1.9 ppm methlylene chloride for a total of 72 hours (table 5). This was done to simulate intermittent real life exposures. The intermittently exposed monitors collected 95% of the amount on the monitors exposed continuously.

TABLE 5

METHYLENE CHLORIDE EXPOSURE AT 1.9 PPM FOR 5 DAYS
ALTERNATING WITH 2 DAYS AT 0 PPM
(72 hours at 1.9 ppm methylene chloride/ 4 days 0 ppm toluene)

ID	mg A	mg B	Total mg
1	0.558	0.185	0.964
2	0.542	0.211	1.006
3	0.569	0.180	0.965
4	0.557	0.172	0.936
5	0.570	0.199	1.007
6	0.539	0.195	0.968

FIELD TEST RESULTS

Our field test was conducted at a 3M pilot plant. Monitoring was conducted for isopropanol and n-butanol from a coating operation over a 3 day time period. The coater operated intermittently. On day 1, it ran for 5 hours. On days 2 and 3 it ran for 12 hours. Monitors were exposed for 1, 2 and 3 days. We used this experiment as another measure of the effects of reverse diffusion. If the back up section contained significant concentrations and the monitors were not near their expected capacity, it would show that reverse diffusion was occurring. As a control we obtained charcoal tube samples on Day 1 and Day 3.

Nine monitors were initially exposed to the n-butanol and isopropanol environment. Three monitors were removed each day and analyzed. The n-butanol results indicated nothing on the back section of any of the monitors. This shows that reverse diffusion of n-butyl alcohol did not occur. See table 6 for summary of n-butanol data.

TABLE 6

n-BUTANOL FIELD TEST

Time	mg	ppm	Average of 3
1737	0.025	0.164	
1737	0.027	0.172	0.166
1737	0.025	0.163	
3255	0.053	0.182	
3255	0.052	0.180	0.185
3255	0.056	0.194	
4715	0.077	0.184	
4715	0.076	0.180	0.182
4715	0.076	0.181	

The results of the isopropanol analysis were somewhat different. On day one we found 65 ug on the front and <1 ug on the back. On day two, 141 ug on the front and 6 ug on the back and on day 3 , 202 ug on the front and 10 ug on the back (see table 7). These results showed that reverse diffusion occurred with isopropanol although the effect was small, and that the use of a monitor with backup was able to provide accurate results. The average air concentration of isopropanol was 0.55 +/-0.07 ppm (+/- 12.7%).

TABLE 7

ISOPROPANOL FIELD TEST

Time	mg A	mg B	Total mg	ppm	Ave of 3
1737	0.065	0.000	0.065	0.461	
1737	0.076	0.000	0.076	0.537	0.498
1737	0.068	0.001	0.070	0.495	
3255	0.155	0.003	0.162	0.611	
3255	0.149	0.004	0.157	0.593	0.594
3255	0.144	0.004	0.153	0.577	
4715	0.216	0.007	0.232	0.604	
4715	0.214	0.007	0.230	0.597	0.599
4715	0.214	0.007	0.229	0.596	

We compared the monitor results with charcoal tubes taken on Day 1 and Day 3 and can see excellent agreement (table 8).

TABLE 8

Diffuison Monitor vs Charcoal Tube

Compound	Monitor (ppm)	Charcoal Tube (ppm)
Isopropanol	0.55 +/- 0.07	0.48 +/- 0.11
n-butanol	0.18 +/- 0.008	0.17 +/- 0.03

CONCLUSIONS

In summary, we can see that the accuracy's ranged from 10% to 17% which are well within the recommended 25%. These experiments show that diffusion monitors can be used for extended sampling periods of one week to one month and still provide acceptable accuracy. When volatile compounds like acetone and methylene chloride are anticipated, it is essential to use the 3M 3520 organic vapor monitor with a backup layer of sorbent to achieve accuracy of 25%.

SUMMARY OF LONG TERM LOW CONCENTRATION EXPERIMENTS

COMPOUND	EXPOSURE TIME (DAYS)	CONC (PPM)	AMOUNT FOUND	AMOUNT EXPECTED	ACCURACY %
Toluene	5 3/4	2.3	1.091 mg	1.088 mg	12.1
1,1,1-TCE	8	0.45	0.86 mg	0.83 mg	14.1
Acetone	5	2.86	1.767 mg	1.97 mg	17.4
Methylene Chloride	5	1.9			13.8
Toluene/MEK	15	0.173/0.028	438.2/68.1 ug	438/64 ug	
Toluene/MEK	21	0.174/0.029	614.9/99.8 ug	618/93 ug	9.8/16.8
Toluene/MEK	28	0.173/0.029	850.5/135.7 ug	827/125 ug	

Comparison of boiling points vs. observations on reverse diffusion leads to the following general recommendation (table 9): the use of a monitor with backup section for those compounds with boiling points below 60 °C and recommending the use of a monitor without a backup for those with boiling points above 90 °C. For those compounds with boiling points between 60 and 90 °C, a monitor with backup would provide higher accuracy with less risk of loss.

TABLE 9

BOILING POINT °C	
N-BUTANOL	118
TOLUENE	111
ISOPROPANOL	82
MEK	80
1,1,1-TRICHLOROETHANE	75
ACETONE	56
METHYLENE CHLORIDE	40

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3M Organic Vapor Monitor Sampling Rate Validation Protocol

Anders, L. W., and H. E. Mullins: Comparison of Diffusional Organic Vapor Monitors with Charcoal Tubes for Sampling Laboratory Challenges to Contaminant Mixtures

Anders, L. W., H. E. Mullins and P. L. Sullivan: Organic Vapor Monitor with Backup Section

Pieper, Richard M., Donald J. Larsen, and Patricia A. Ishaug: STEL Sampling Using Diffusional Monitors, American Chemical Society Meeting, Boston, MA, April, 1990.

Epstein, Paul S., et al: Experiences Using Passive Monitors to Measure Volatile Organic Compounds During Indoor and Ambient Air Quality Surveys, American Industrial Hygiene Conference, 1990.

Cohen, Martin A., et al: The Validation of a Passive Sampler for Indoor and Outdoor Concentrations of Volatile Organic Compounds, J. Air Waste Manage. 40:993(1990).

ORGANIC VAPOR MONITOR WITH BACKUP SECTION #3520

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Introduction

The 3M Brand Organic Vapor Monitor #3520 with backup section is a diffusionally controlled sampling device designed to measure time-weighted-average concentration of potentially hazardous organic vapors in the environment. The sample is equipped with a backup section which collects contaminants when the capacity of the primary adsorbent has been exceeded. The monitor consists of two layers of adsorbent medium separated by a small space containing a placid air layer within the monitor. The amount of contaminant collected by the primary adsorbent layer is determined by sampling time and contaminant concentration in the environment. For a specific contaminant, the secondary adsorbent begins to collect contaminant by diffusion when the capacity of the primary adsorbent is exceeded for that particular contaminant. The capacity can be exceeded when sampling contaminant mixtures, contaminants at high concentrations, as well as contaminants for which activated carbon has a low capacity. By comparing the weight collected on each of the adsorbents (primary and secondary), the validity of the sample collected by the monitor can be determined. If the sample is determined to be valid, then the weight of contaminant on the primary and secondary adsorbent is used to calculate the time-weighted-average concentration of the contaminant in the environment during the sampling period.

Principle of the Method

The 3M Brand Organic Vapor Monitor #3520 with the backup section is a personal sampler to be worn near the breathing zone of the worker. The sampler collects contaminants from the ambient atmosphere by diffusion onto the primary adsorbent where it is collected. The weight collection rate is a linear function of the exposure (product of the concentration and time). As the primary adsorbent collects contaminant, the collection rate will eventually deviate from the linear relationship. The adsorbent's capacity for the contaminant is defined as the weight adsorbed when the above deviation occurs. When the capacity of the primary adsorbent is reached with the 3520 Organic Vapor Monitor, the contaminant then diffuses to the secondary adsorbent in the backup section. Because of the geometric dimensions, the sampling rate of the contaminant onto the secondary adsorbent is 45% of the sampling rate onto the primary adsorbent.

Upon analysis of each adsorbent, the validity of the sample can be determined. Because the mass of activated carbon in the primary adsorbent is equivalent to the mass of activated carbon in the secondary adsorbent, the contaminant capacity on each should be equivalent. But in order to assure a valid sample under all sampling conditions, the ratio of the contaminant weight (W_s) on the secondary adsorbent to the contaminant weight (W_p) on the primary adsorbent must meet the following criteria.

$$\frac{W_s}{W_p} \leqslant .50$$

When sampling an environment containing multiple contaminants with the 3520 Organic Vapor Monitor, the above criteria can be used to determine the sample validity of each contaminant. Therefore, for those contaminants which fulfill the above criteria, the weight (W_p) on the primary adsorbent and the weight (W_s) on the secondary adsorbent can be used to accurately determine the time-weighted-average concentration.

The weight corrected for the blank of each contaminant on the primary and secondary adsorbent (W_p and W_s) can be used to calculate the time-weighted-average concentration according to the following equation:

$$C\ (mg/m^3) = \frac{W_p}{K_p \times t} + \frac{W_s}{K_s \times t}$$

W_p - corrected weight collected on the primary adsorbent

W_s - corrected weight collected on the secondary adsorbent

K_p - sampling rate of the contaminant onto the primary adsorbent

K_s - sampling rate of the contaminant onto the secondary adsorbent

t - length of sampling period

The above equation can be simplified to the following:

$$C\ (mg/m^3) = \frac{W_p + kW_s}{K_p \times t}$$

where,

k - A constant determined by the ratio K_p/K_s. For all contaminants, this ratio has been determined to be a constant value of 2.2.

With this simplification, the time-weighted-average concentration of the contaminant in the environment can be calculated from the corrected weight collected by the primary and secondary adsorbent, the length of the sampling period and contaminant sampling rate onto the primary adsorbent.

The geometric dimensions (area and length) of the primary diffusional chamber for the 3520 Organic Vapor Monitor with the backup section are the same as the dimensions of the diffusional chamber for the 3500 Organic Vapor Monitor. Therefore, the sampling rates (K_p) for contaminants onto the primary adsorbent of the 3520 Organic Vapor Monitor are the same as those tabulated in the Sampling and Analysis Guide for the 3500 Organic Vapor Monitor.

As the diffusional capacity of the primary adsorbent is reached with the 3520 Organic Vapor Monitor and the secondary adsorbent starts to collect contaminant, it is merely an indication that for the primary adsorbent, the weight collection rate is no longer a linear function of the exposure. Although the diffusional capacity for the primary adsorbent may be reached during sampling, the adsorbent will continue to collect contaminant even though the weight collection rate deviates from the linear relationship. As will be shown later, the weight (W_p) collected on the primary adsorbent even though in excess of the defined capacity can be combined with the weight (W_s) collected on the secondary adsorbent to give an accurate determination of the time-weighted-average concentration in the sampled environment. These weights (W_p and W_s) can be combined according to the above expression as long as the ratio W_s/W_p complies with the above criteria. Therefore, the 3520 Organic Vapor with the backup section increases the effective sampling capacity by a factor of at least four over the 3500 Organic Vapor Monitor capacity. This allows the recommended sampling periods tabulated in the Sampling Guide for the 3500 Organic Vapor monitor to be increased by at least four times when sampling with the 3520 Organic Vapor Monitor.

To insure proper operation of the secondary section according to the given criteria, immediately separate the primary and secondary sections after sampling is terminated. Conclusion of sampling occurs when the white face of the monitor and the retaining ring are removed and the closure cap is snapped in place. Next, the primary and secondary sections are separated. The brown cap is snapped into place on the bottom of the primary section and the other closure cap is snapped on the secondary section. The two ports in the cap are firmly closed with the attached plugs. The improtance of these final steps should be emphasized since environmental sampling continues until the bottom brown cup and the closure are on with all ports closed.

Documentation of Sampling Performance

The 3M Brand Organic Vapor Monitor #3520 with the backup section is a diffusional sampling device which allows the industrial hygienist to determine sample validity. It is very valuable to assure sample validity when sampling an environment with a mixture of contaminants as well as contaminants at high concentrations. Besides assuring sample validity when sampling contaminants such as acetone, methylene chloride, vinyl chloride, etc. for which the activated carbon has a low capacity, the #3520 Organic Vapor Monitor also extends the effective sampling capacity and enables the recommended sampling periods to be increased. The following table is a list of eight commonly sampled contaminants which not only have high Permissible Exposure Level (PEL's) but also have limited capacity for activated carbon. From the table, it can be observed that the recommended sampling times can be extended in most instances to allow full work shift sampling.

TABLE I

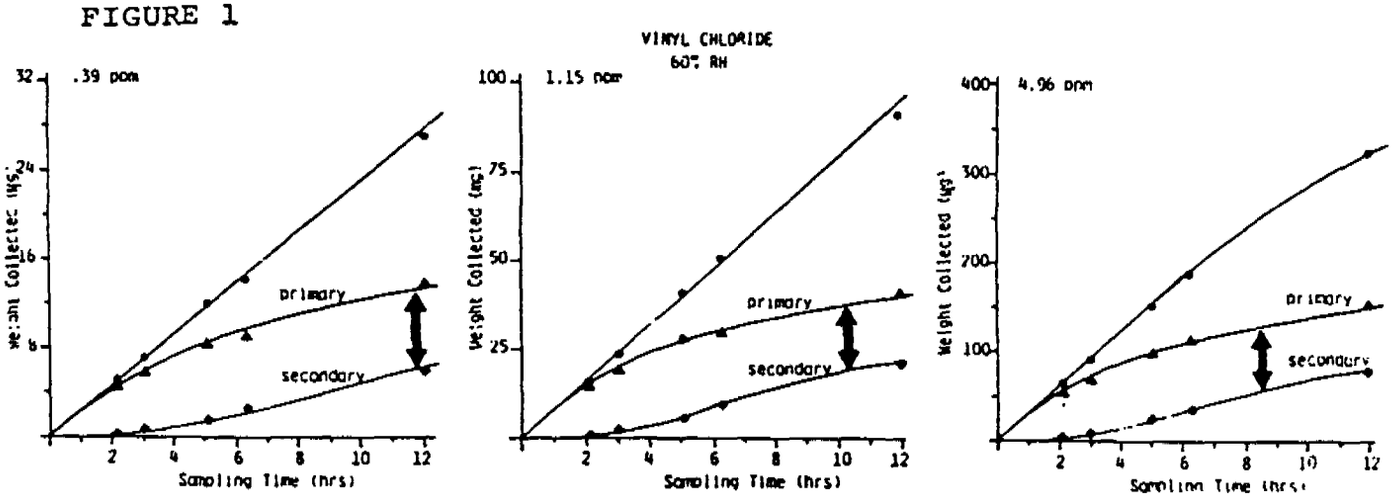
	OSHA PEL (ppm)	Sampling Rate $\left(\frac{\text{Micrograms}}{\text{ppm-hrs}}\right)$	Primary Adsorbent Capacity (mg)	Recommended Sampling Period for 3520 OVM (hours) Concentration x PEL .1X	.5X	1X	3X
Acetone	1,000	5.71	3	8	4	2	1
Ethyl acetate	400	7.45	10	8	8	8	5
Ethyl ether	400	6.68	.4	6	1	.6	.2
Methyl acetate	200	6.72	2	8	8	6	2
Methyl chloroform	350	10.09	12	8	8	8	5
Methyl chloride	500	7.91	2	8	4	2	1
Pentane	1,000	5.56	7	8	8	5	2
Vinyl chloride	1	6.22	.04	8	8	8	8

To document the incr ase in effective sampling capacity, a number of contaminants from the above table were selected to be evaluated by sampling a laboratory chall nge of known concentration. In Figure 1, vinyl chloride was sampled at three concentrations (.39, 1.15 and 4.96 ppm) at a relative humidity of 60%. The double arrow between the primary and secondary curve indicates where the ratio W_s/W_p is equal to .50. Therefore, it is the point beyond which the sample would be considered to be invalid. The response line of the 3520 was obtained from the combined weight (W_c) of the weight (W_p) on the primary adsorbent and the weight (W_s) on the secondary adsorbent according to the following equation.

$$W_c = W_p + 2.2\ W_s$$

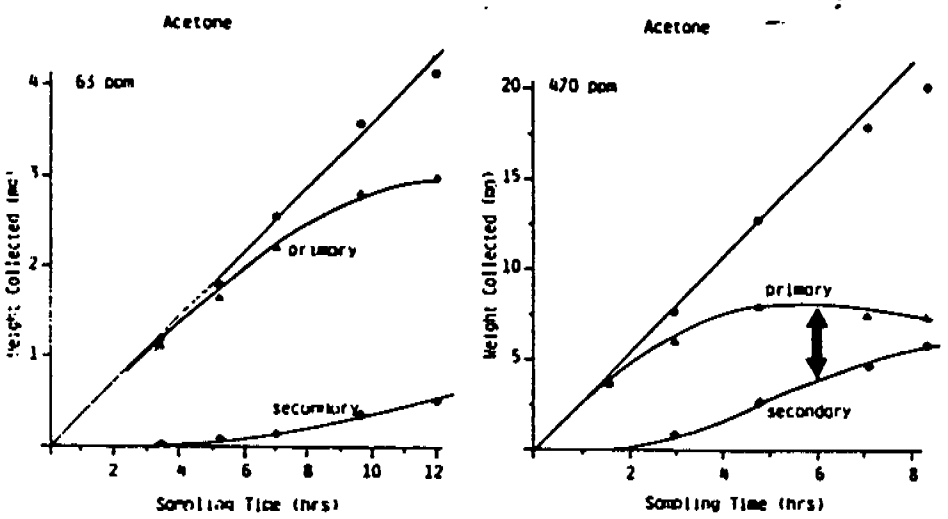
It can be observed that the response of the 3520 as measured by the combined weight (W_c) is linear beyond the point of the double arrow and also that the sampling time at all concentrations can be in excess of eight hours.

FIGURE 1



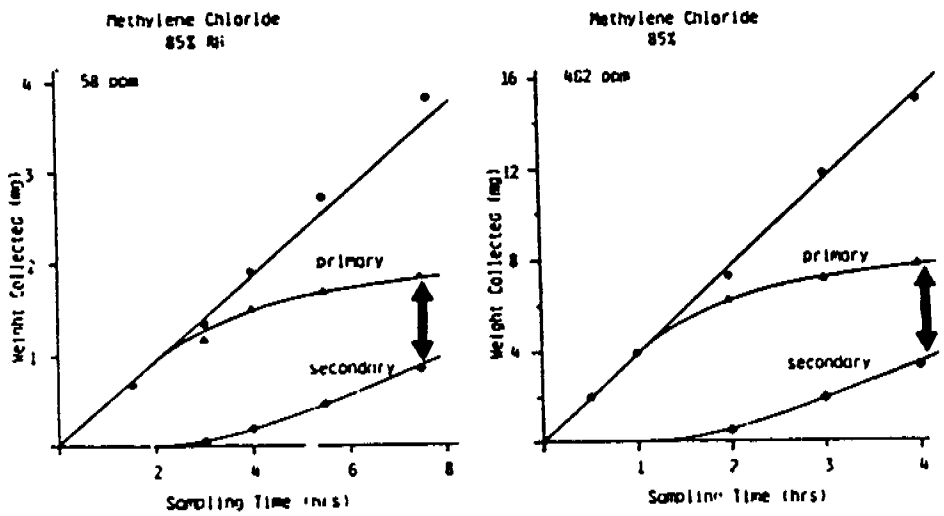
In Figure 2, acetone was sampled from known challenges of 63 and 470 ppm. At the lower concentration it can be observed that a valid sample was collected through the entire 12 hour sampling period while at the higher concentration after six hours of sampling the sample was invalid. Although, it should be pointed out that after eight hours, the response of the 3520 OVM as measured by the combined weight (W_c) deviated only slightly from the expected linear response.

FIGURE 2



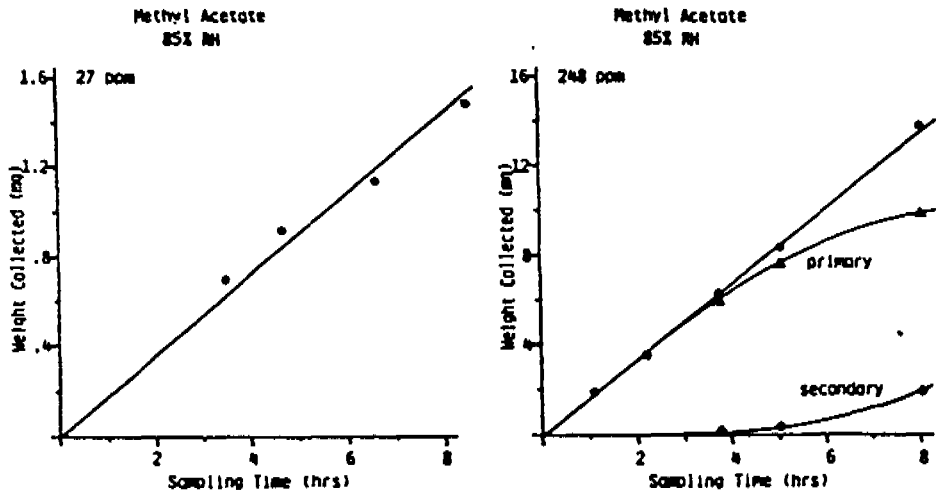
In Figure 3, methylene chloride was sampled from known challenges of 58 and 482 ppm at a relative humidity of 85%. Again, the double arrow indicates the point beyond which an invalid sample would be collected as determined by the above criteria of weight ratio. As expected the response of the 3520 OVM as measured by the combined weight (W_c) gives the expected linear relationship between weight and the sampling time at known constant challenges.

FIGURE 3



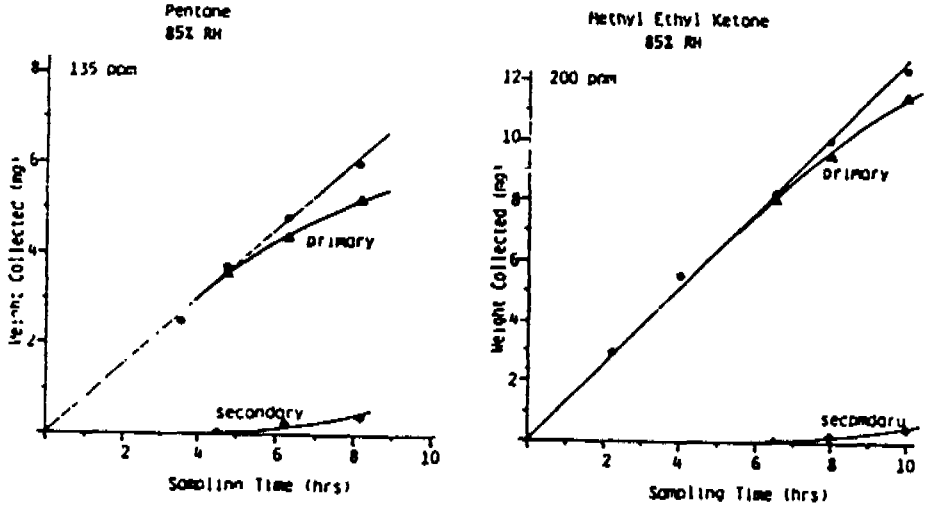
In Figure 4, methyl acetate was sampled from known challenges of 27 and 248 ppm. From the results it can be observed that at both challenges a valid sample was collected through the eight hour sample periods.

FIGURE 4



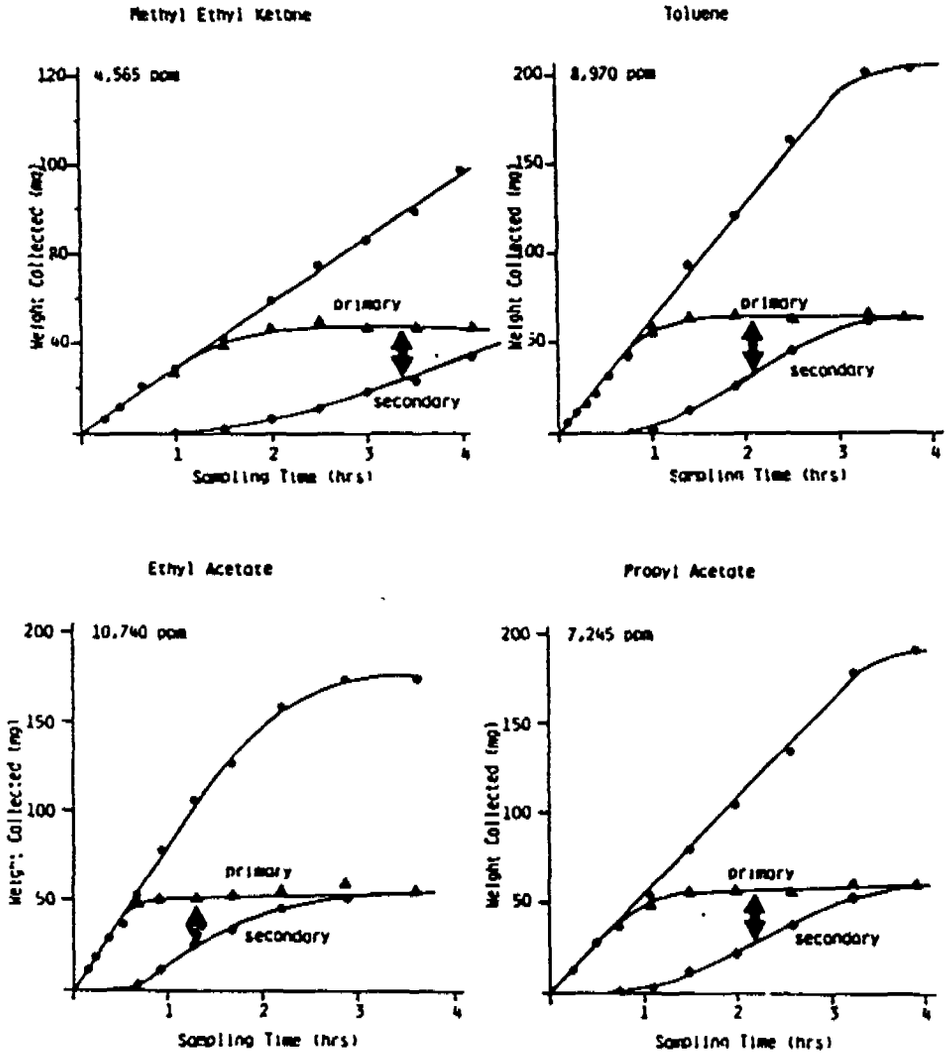
In Figure 5, pentane and methyl ethyl ketone were sampled from challenges at concentrations of 135 and 200 ppm respectively. In both cases very little sample was collected by the secondary adsorbent during the sampling periods.

FIGURE 5



As was pointed out earlier, the 3520 OVM is also able to determin sample validity when sampling at very high concentrations. In Figure 6, MEK, toluene, ethyl acetate and propyl acetate were sampled from challenges where the known concentrations were very high. The double arrow again indicates the point beyond which the sample should be considered to be invalid. The response of the 3520 OVM as measured by the combined weight (W_c) is linear even past the double arrow.

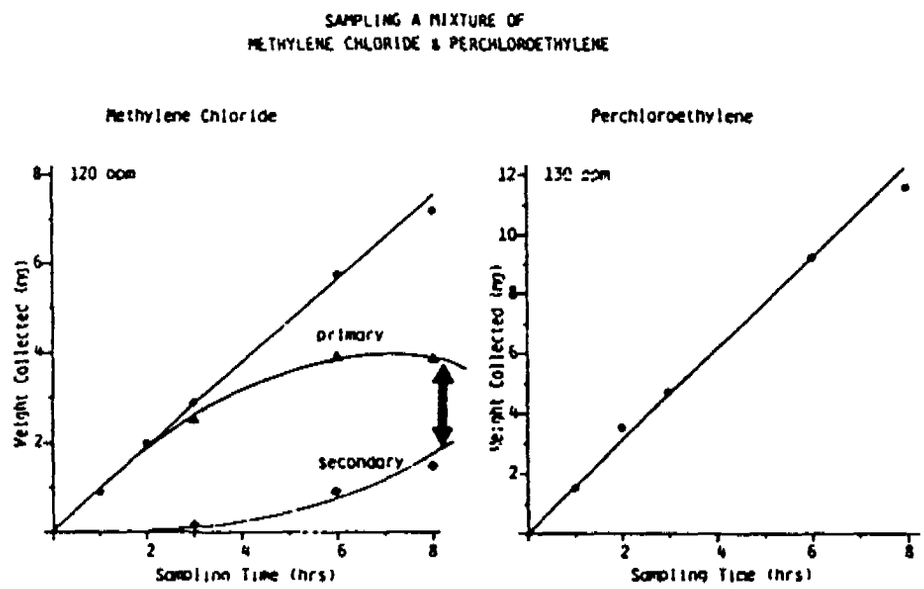
FIGURE 6



From the above results where the 3520 OVM sampled known challenges of a single contaminant, it has been shown that sample validity can be determined from a realistic criteria defined by the ratio of the weight collected on the secondary adsorbent to the weight collected on the primary adsorbent. It also has been shown that the effective capacity of the sampling device is greater than four times the capacity for a sampling devic containing only a single adsorbent. This increased effective capacity allows longer sampling periods when sampling contaminants with a low capacity on activated carbon.

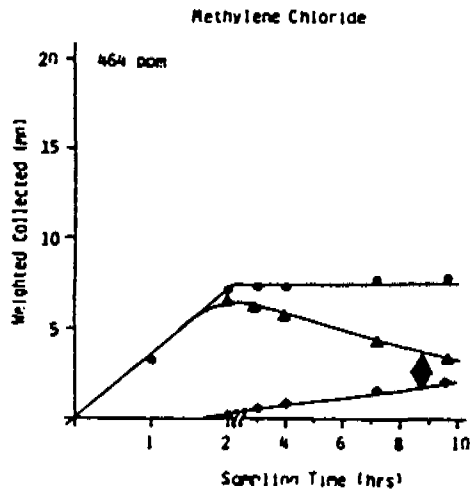
As was indicated above, the 3520 OVM is also very valuable to determine sample validity when sampling environments containing more than one contaminant. First the performance of the 3520 OVM was documented by sampling known changes of a two component mixture. In Figure 7, a mixture of methylene chloride and perchloroethylene at concentrations of 120 and 130 ppm respectively was sampled. As expected, the methylene chloride, for which the activated carbon has a low capacity, was collected on both the primary and secondary adsorbent. The perchloroethylene was collected only on the primary adsorbent of the 3520 OVM. The double arrow again indicates the point where the ratio W_s/W_p is equal to .50.

FIGURE 7



In Figure 8, methylene chloride was sampled from a 464 ppm challenge for two hours. This was followed by a challenge containing a zero concentration of methylene chloride. It is evident that the primary adsorbent collected methylene chloride in excess of its capacity. Although the primary adsorbent lost methylene chloride during this period, the secondary adsorbent collected the appropriate amount from the primary adsorbent. The response of the 3520 as measured by the combined weight gave an accurate measure of the concentration sampled.

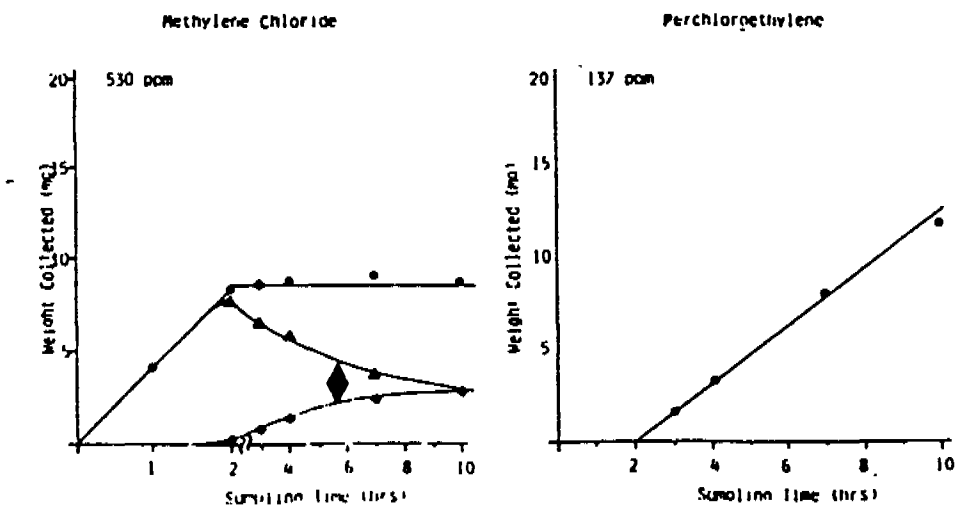
FIGURE 8



In Figure 9, methylene chloride was again collected in excess of the capacity of the primary adsorbent. After the methylene chloride was sampled during the first two hours, a challenge of perchloroethylene was sampled for eight hours. During this period, the methylene chloride was displaced from the primary adsorbent. Again the response of the 3520 as measured by the combined weight gave an accurate measure of the concentration sampled for each of the contaminant.

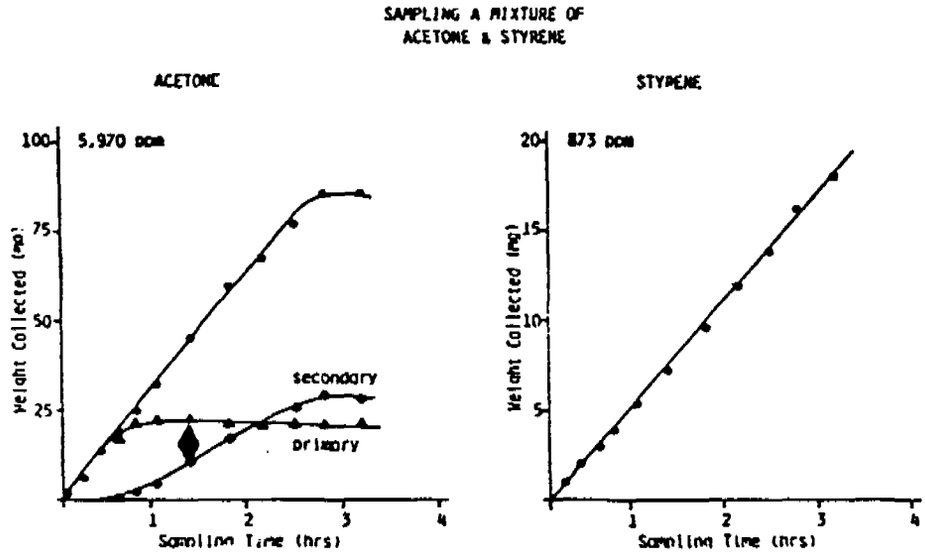
FIGURE 9

SEQUENTIAL SAMPLING OF
METHYLENE CHLORIDE ON PERCHLOROETHYLENE



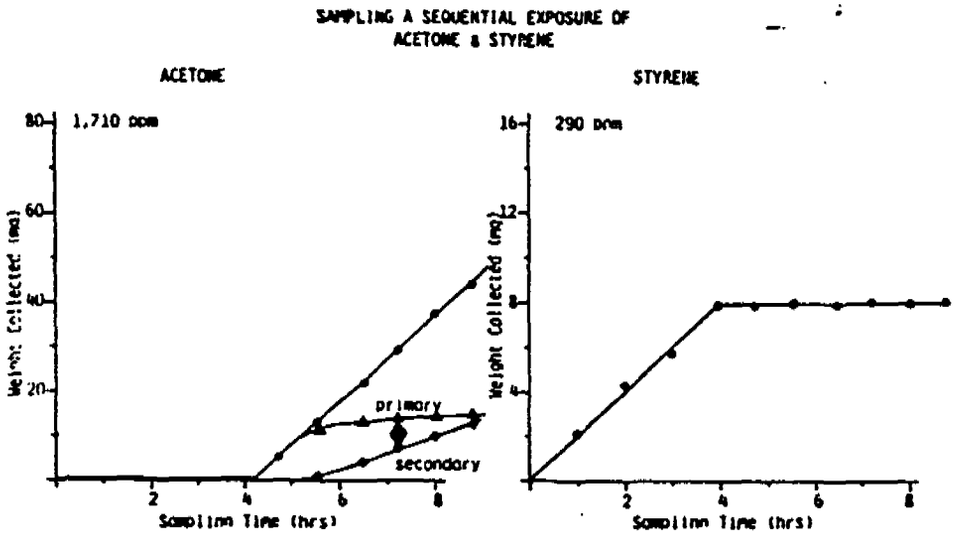
A mixture of acetone and styrene is often found in many industrial environments. In Figure 10, these two contaminants were sampled from laboratory challenges of 5970 and 873 ppm respectively. These were certainly very high concentrations, but valid samples were collected even in excess of the limit imposed by the validity criteria. It is interesting to point out that the secondary adsorbent collected more acetone than the primary adsorbent. This occurred because part of the capacity of the primary adsorbent was used by the adsorbed styrene.

FIGURE 10



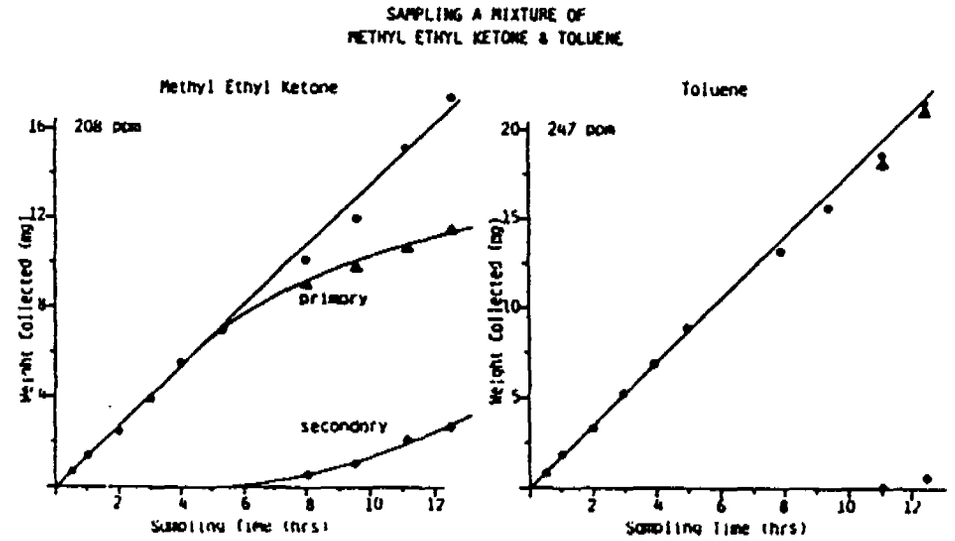
In Figure 11, instead of sampling acetone and styrene simultaneously from a mixture, the 3520 OVM was used to sequentially sample a known challenge of styrene for four hours then a known challenge of acetone for five hours. With styrene, the sample was valid because no contaminant was ever collected on the secondary adsorbent. For acetone, the sample would have been judged to be valid through seven hours of sampling by comparing the ration of W_s/W_p, but it is interesting that the 3520 OVM gave a linear response during the entire nine hour sampling period.

FIGURE 11



Methyl ethyl ketone and toluene is another mixture often found in the industrial environment. In Figure 12, valid samples were collected through 12.5 hours when a known challenge of 208 and 247 ppm respectively

FIGURE 12



In Figure 13, the same mixture was sampled from a challenge with even higher concentrations of both methyl ethyl ketone and toluene. The response of the 3520 as measured by the combined weight (W_c) is again linear even past where the weight ratio criteria has been exceed.
When sampling the high concentration of this mixture, it can be observed that methyl ethyl ketone was displaced from the primary adsorbent by the toluene during latter portion of the sampling. This is evident by observing that the methyl ethyl ketone weight collected on the primary adsorbent decreases after one hour of sampling while the weight on the secondary continues to increase. Even though the displacement occurred, the combined weight as determined according to the above equation from the weight collected by the primary and secondary still gives the expected linear response as a function of sampling time.

FIGURE 13

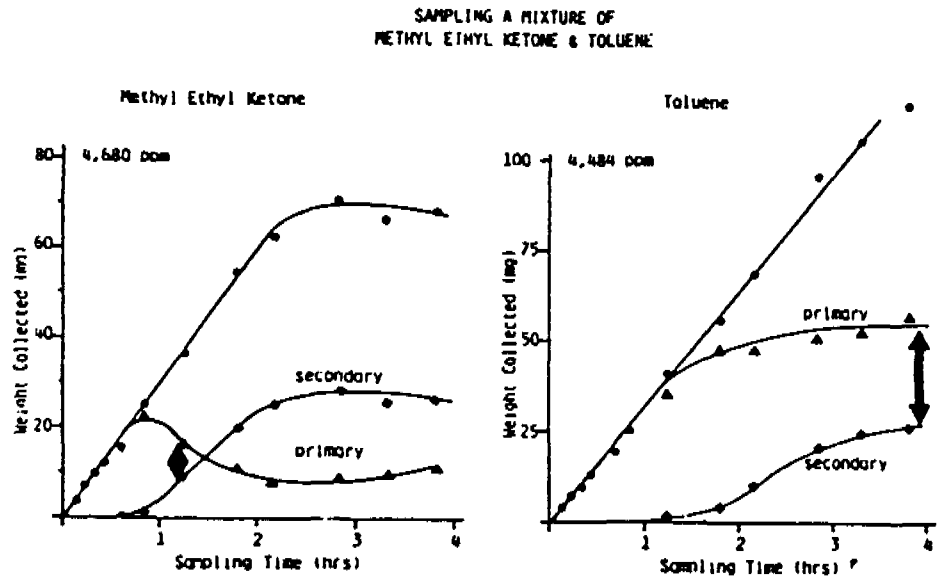
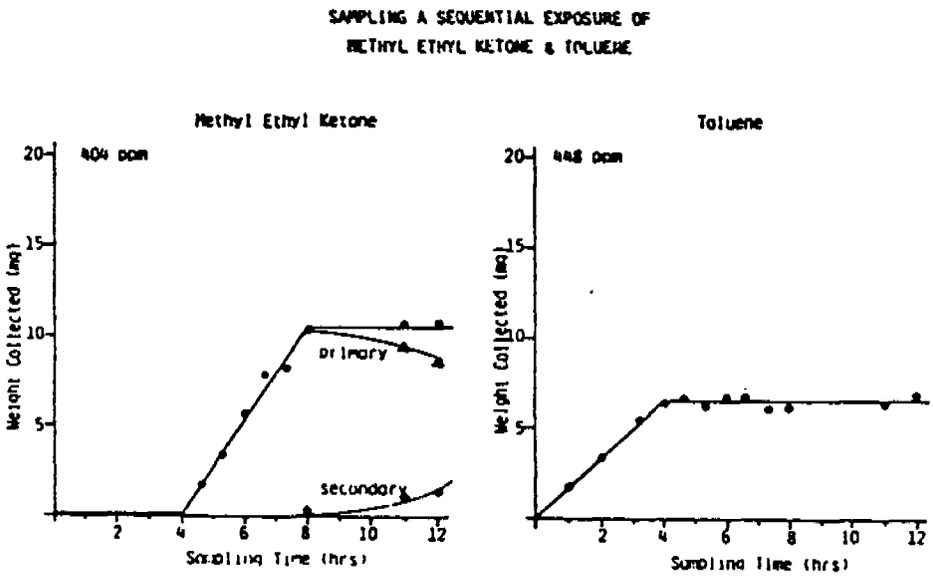


Figure 14 is another example of sequentially sampling a known challenge. Toluene was sampled for four hours with all the contaminant collected only on the primary adsorbent. Methyl ethyl ketone was sampled for the following four hours and all of the contaminant was collected on the primary adsorbent. During the next four hours, the sampling devices were exposed to air with a zero challenge of each contaminant. It is evident that some methyl ethyl ketone was lost by the primary adsorbent during this period, but with the secondary adsorbent present, the 3520 response as measured by the combined weight accurately indicated the weight collected during the sampling of the known challenge.

FIGURE 14



In the next set of laboratory evaluations to document the performance of the 3520 OVM, challenges of three sets of contaminant mixtures were sampled. The mixtures consisted of a group of ketone, a group of esters and a group of halogenated compounds. In Figure 15, 16, and 17, the mixture consisted of acetone, methyl ketone and methyl isobutyl ketone. Three sets of challenges each with increased concentration of the contaminants were sampled. These ketones were selected because of the capacity range activated carbon has for these contaminants. It should be indicated that sample validity can be judged for each contaminant independent of the response of the 3520 for the other contaminants present in the challenge being sampled.

FIGURE 15

SAMPLING A MIXTURE OF
THREE KETONES AT 85% RH

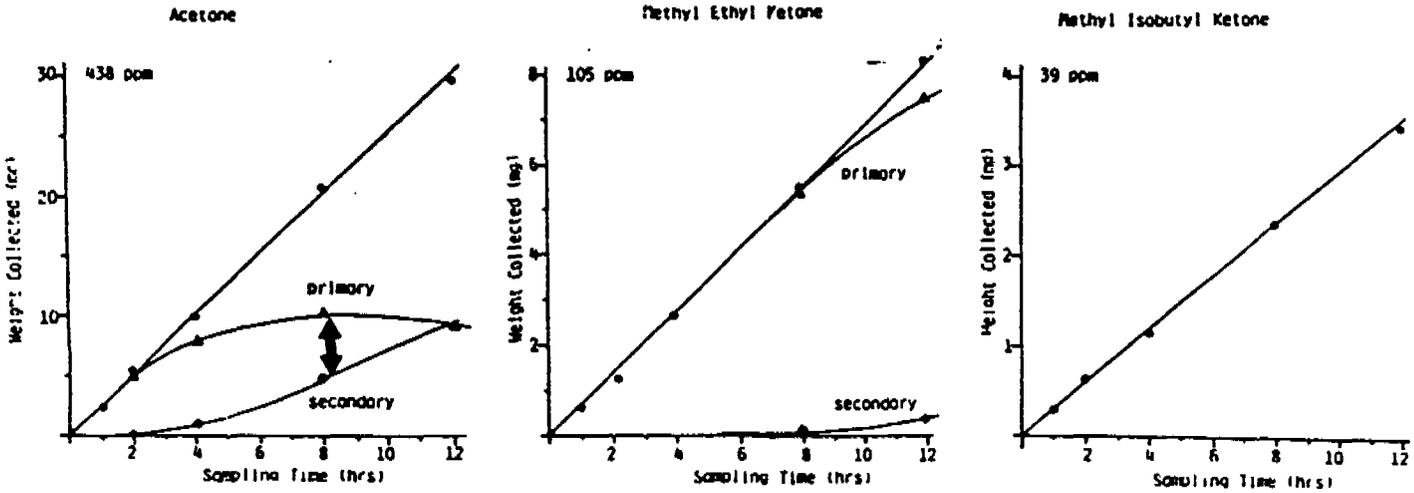


FIGURE 16

SAMPLING A MIXTURE OF
THREE KETONES AT 85% RH

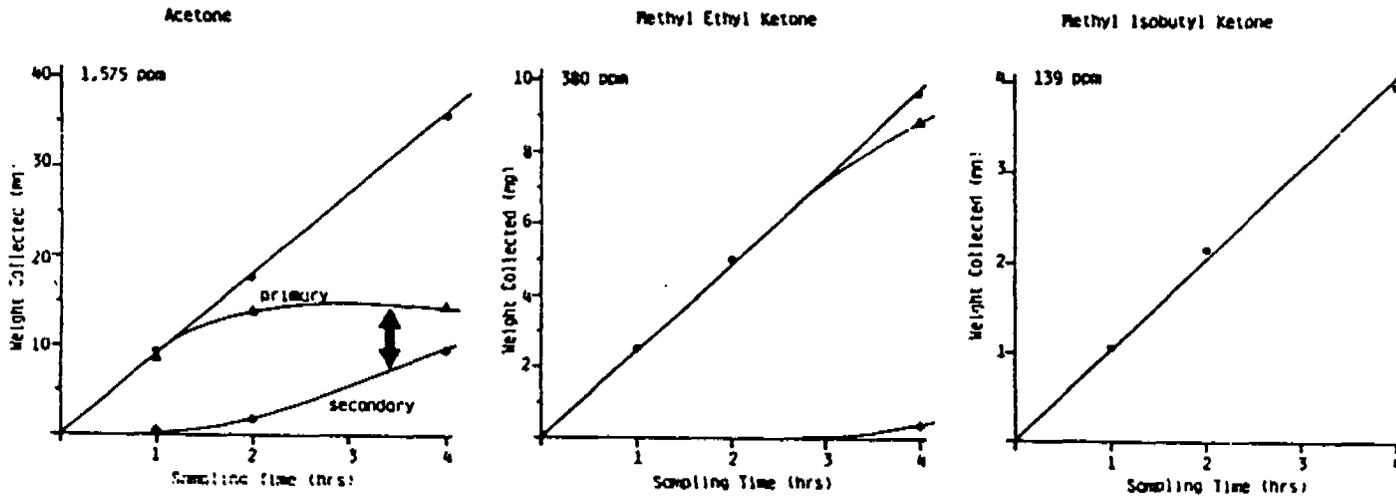
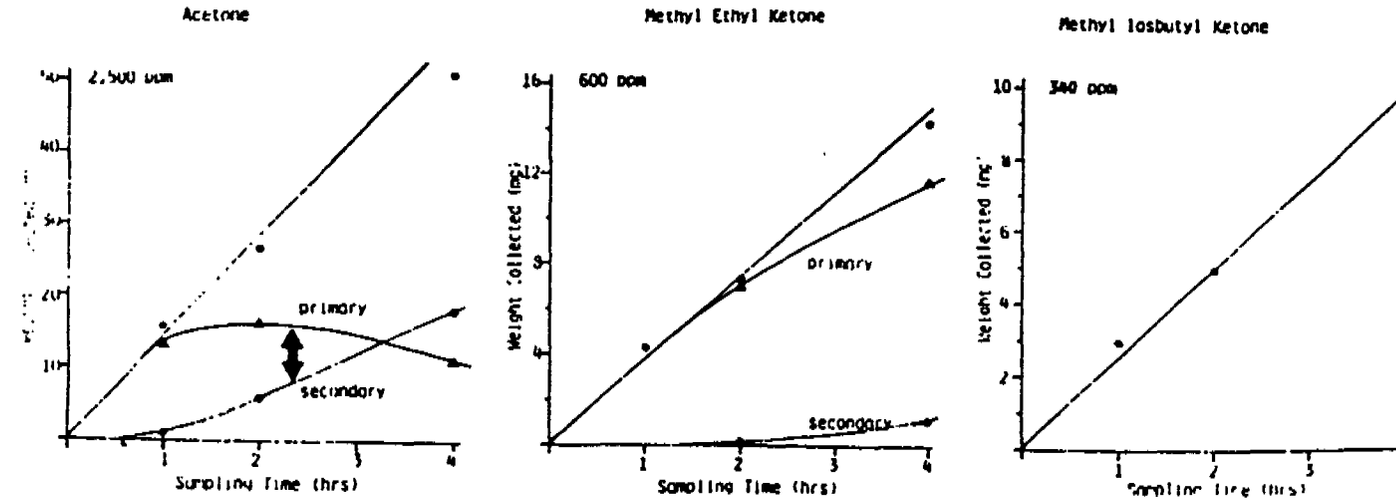


FIGURE 17

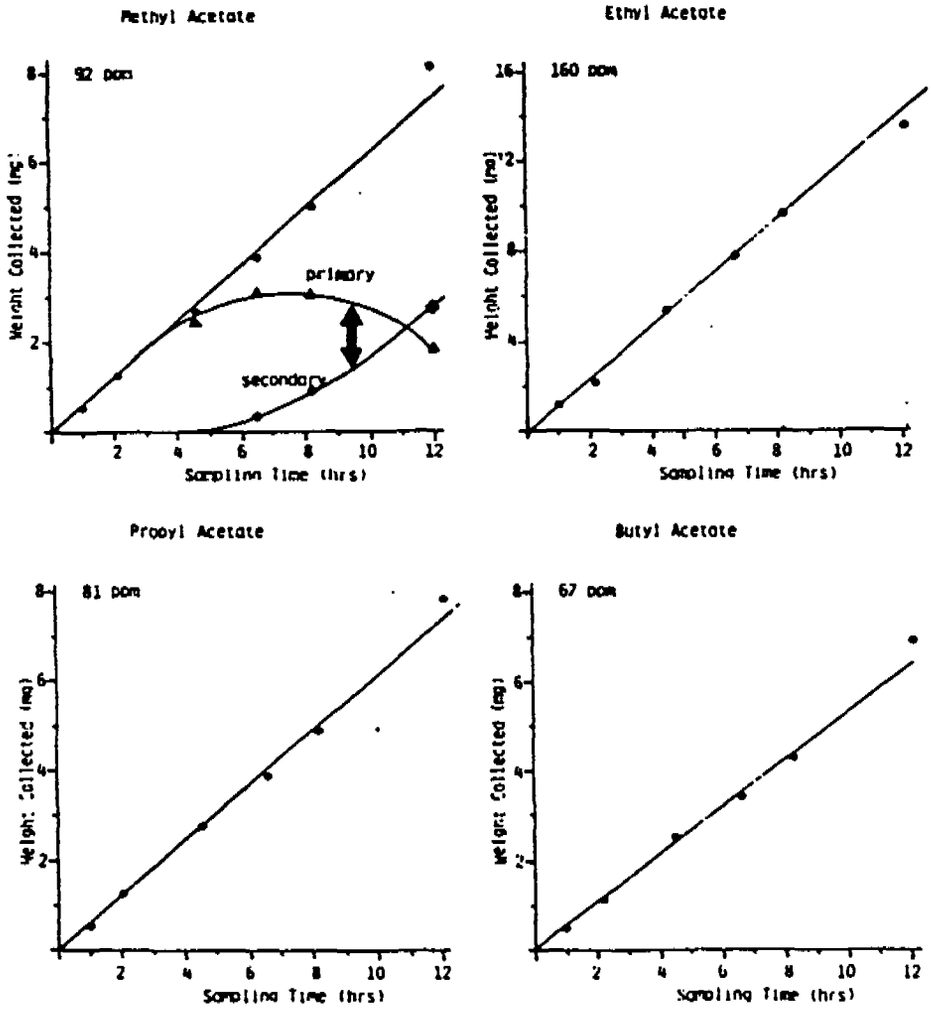
SAMPLING A MIXTURE OF
THREE KETONES AT 85% RH



The next mixture consisted of a group of esters again selected because of the capacity range the activated carbon has for these four contaminants. In Figure 18, at the lowest challenge concentration, only methyl acetate was collected on the secondary adsorbent and the samples were valid for all contaminants for at least a nine hour sampling period.

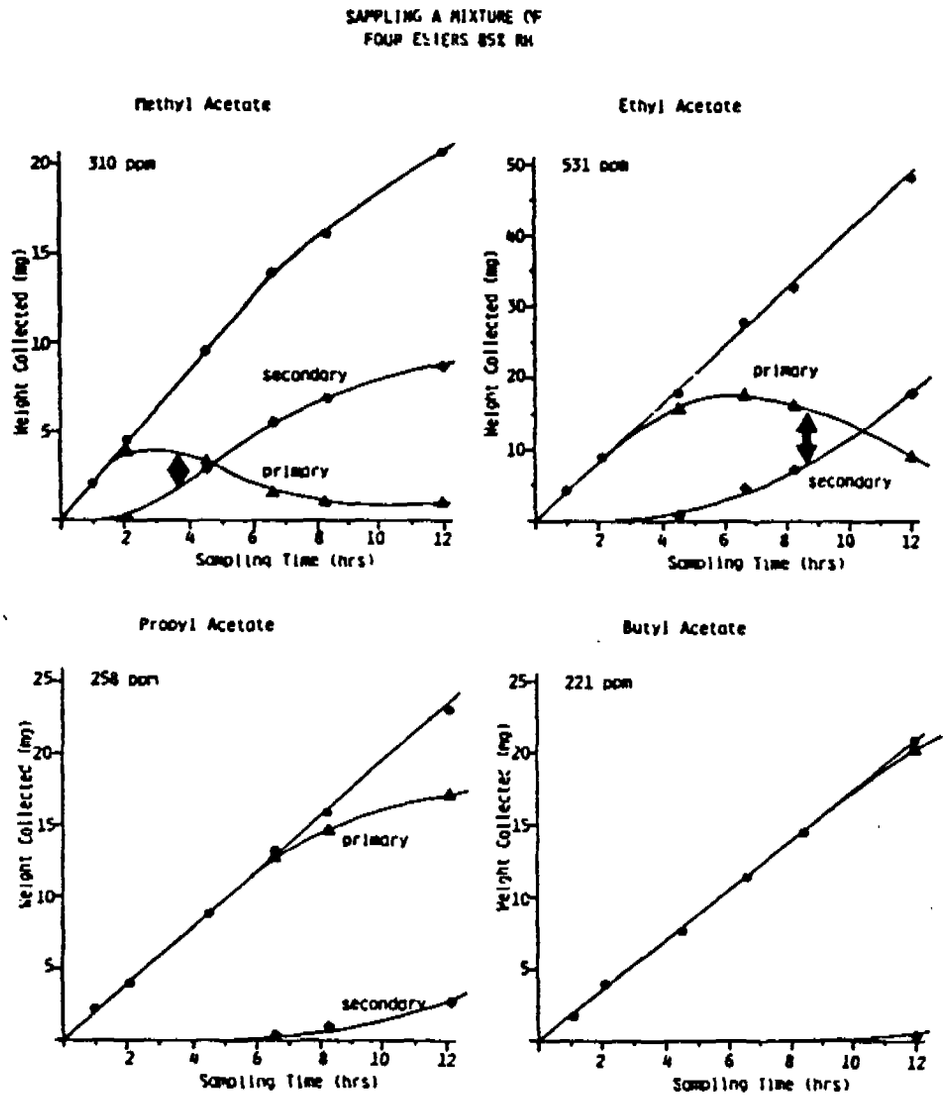
FIGURE 18

SAMPLING A MIXTURE OF FOUR ESTERS 05% RH



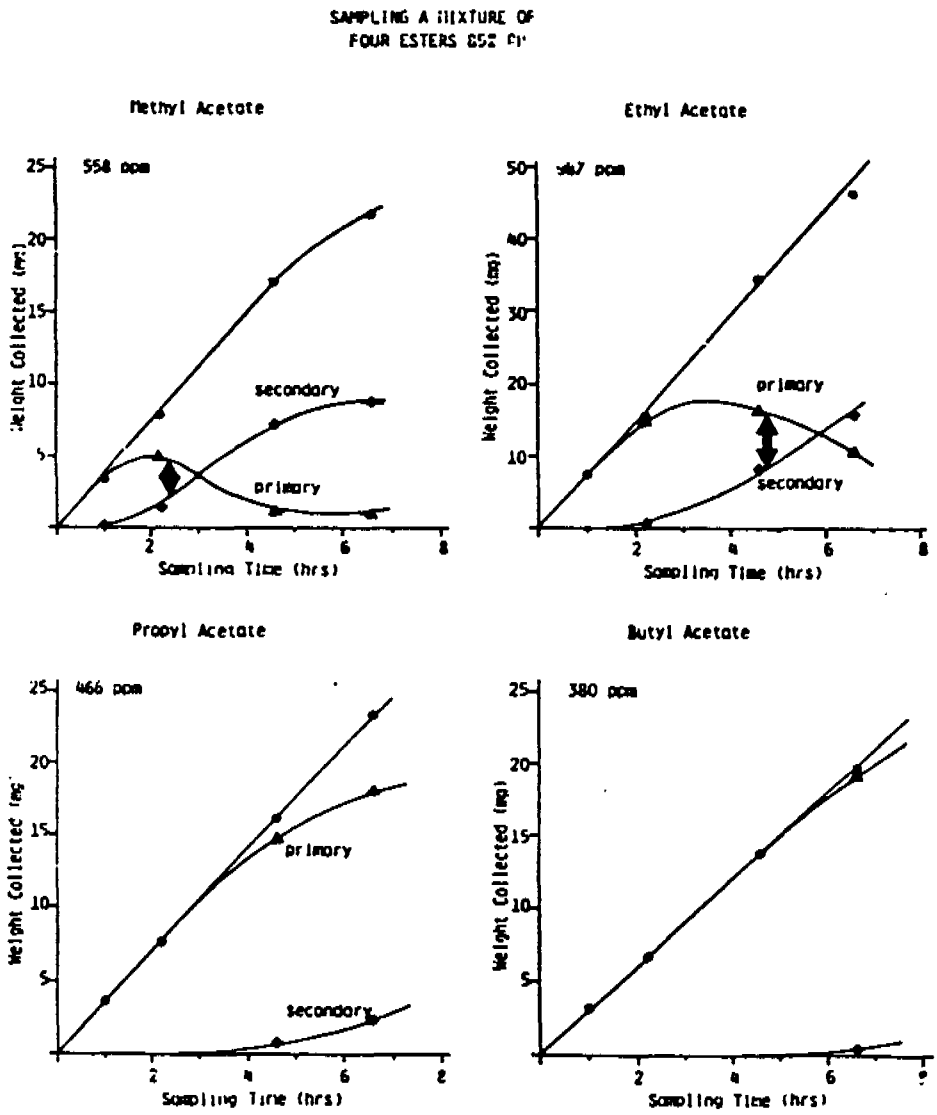
In Figure 19, with the same esters at higher concentrations, the secondary adsorbent collected even butyl acetate after 12 hours of sampling. It is important to indicate again that the 3520 respons as measured by the linear response of the combined weight was excellent even past the point of the double arrows.

FIGURE 19



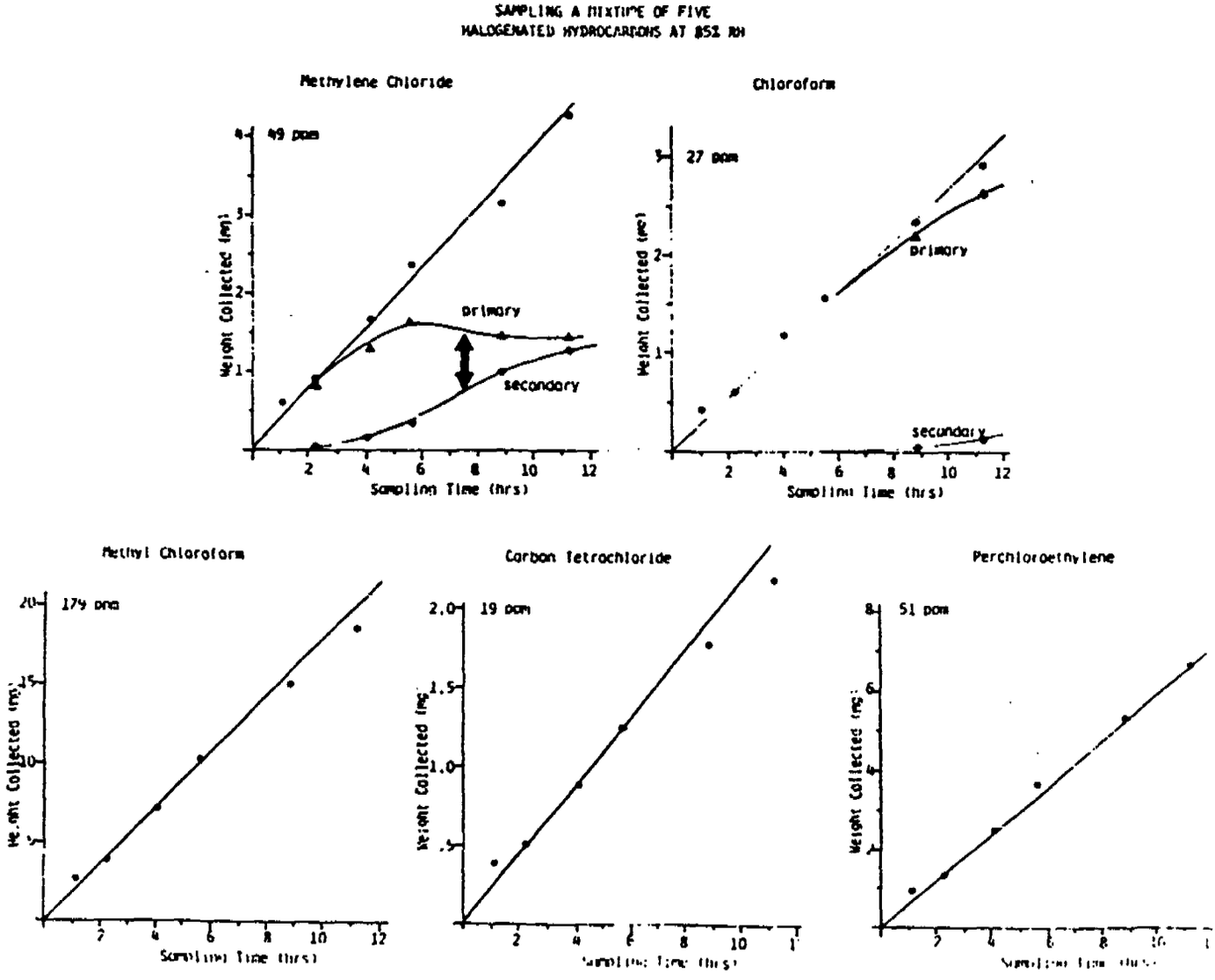
In the above figure as well as in Figure 20, where the same contaminants are sampled even at higher concentration, the displacement of methyl acetate and ethyl acetate from the primary adsorbent occurred during the latter part of the sampling period. But because of the secondary adsorbent, the combined weight gave the expected linear response even past the point where the samples were determined to be valid.

FIGURE 20



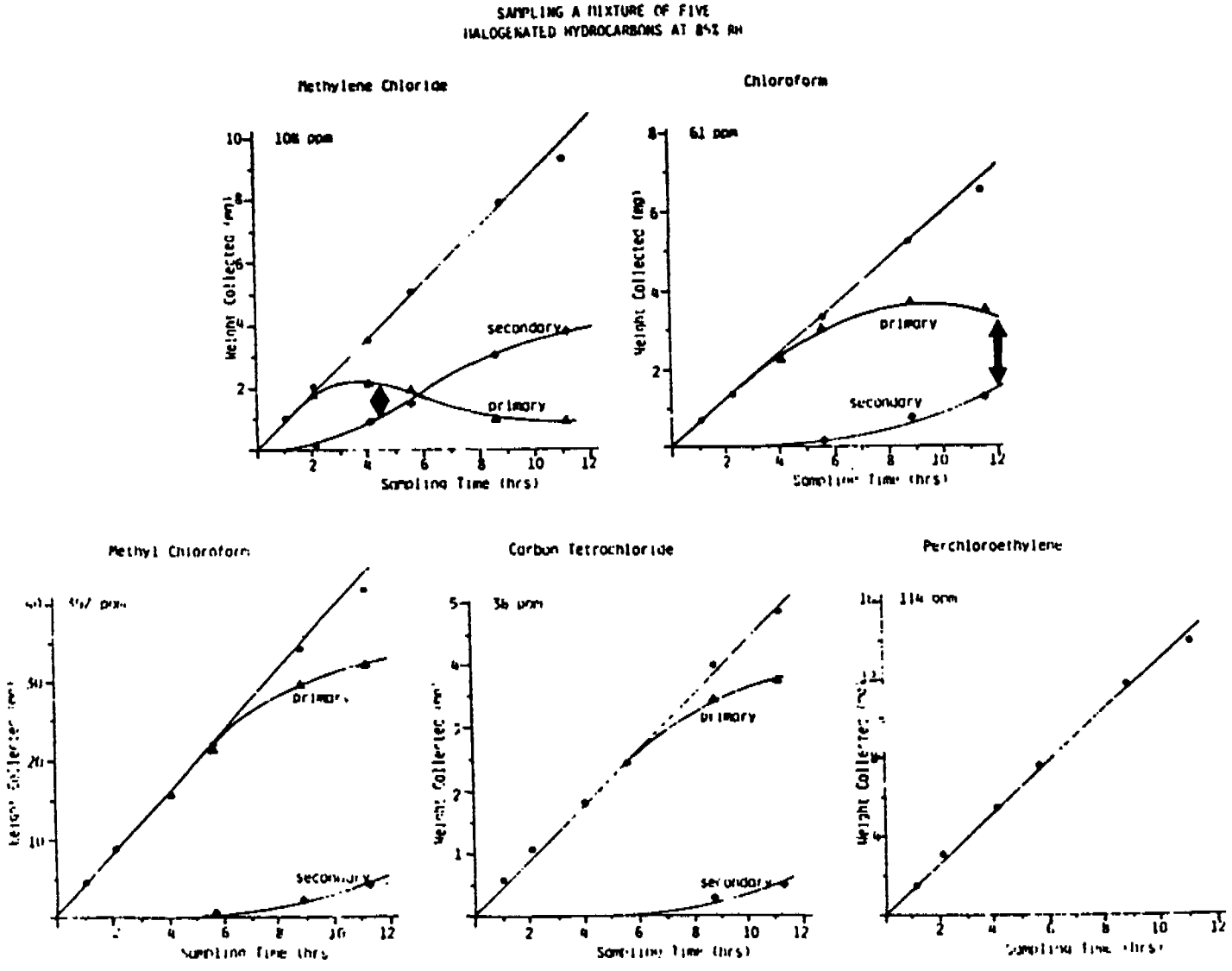
In the next three figures, the 3520 sampled known chall nges of a mixture consisting of five halogenated hydrocarbons. In Figure 21, valid samples were collected for twelve hours for all of the contaminants except for methylene chloride. For methylene chloride, the sample was valid for a seven hour sampling period when judged by the weight ratio of the contaminant collected on the secondary and primary adsorbent.

FIGURE 21



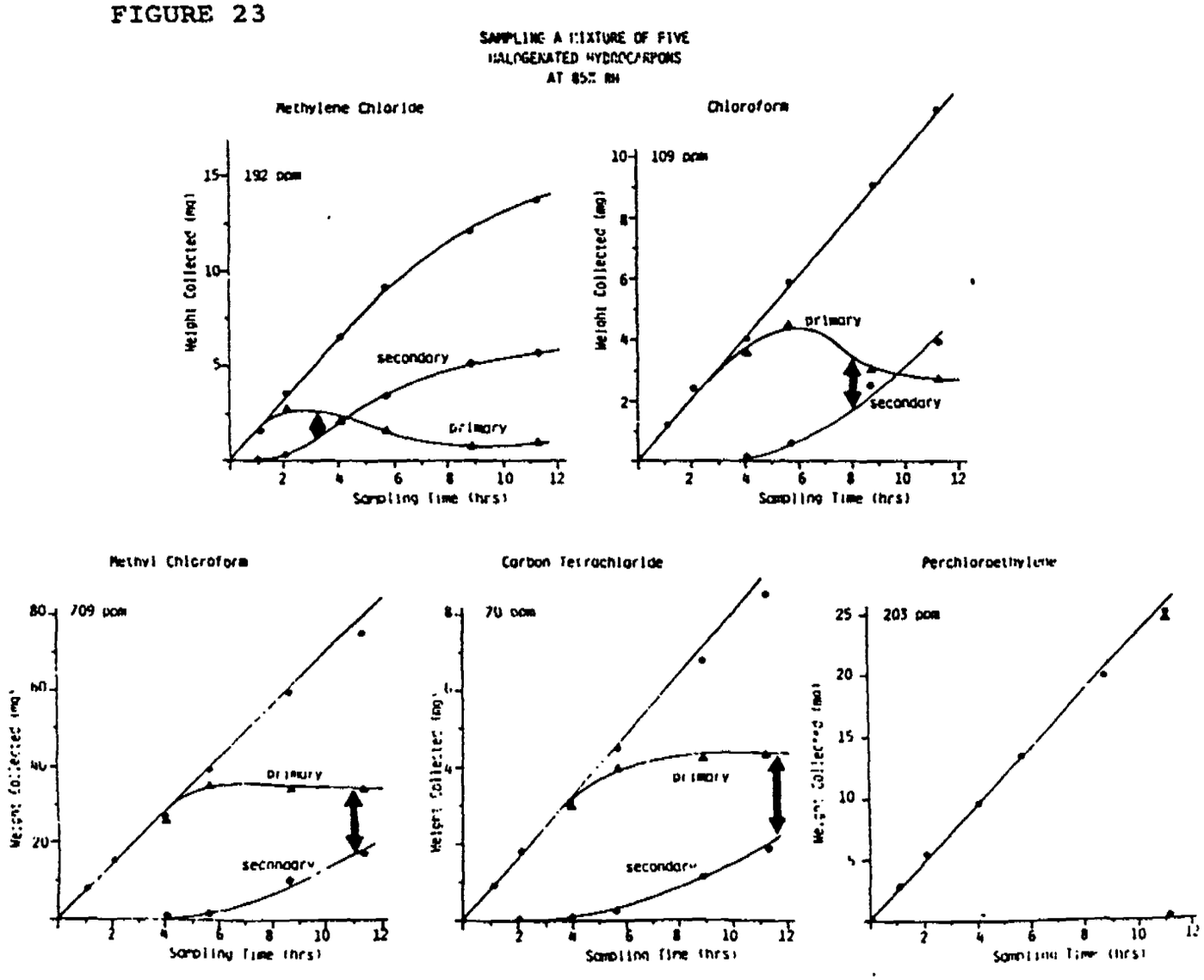
In Figure 22, the same contaminant mixture was sampled at somewhat higher challenge concentrations. Again, the contaminant with the lowest capacity,in this case methylene chloride, was displaced from the primary adsorbent during the latter portion of the sampling period. Even though displacement occurred and sample validity according to the weight ratio criteria was exceeded past a four hour sampling period, it can be observed that all contaminants were sampled accurately for the entire 12 hour sampling period.

FIGURE 22



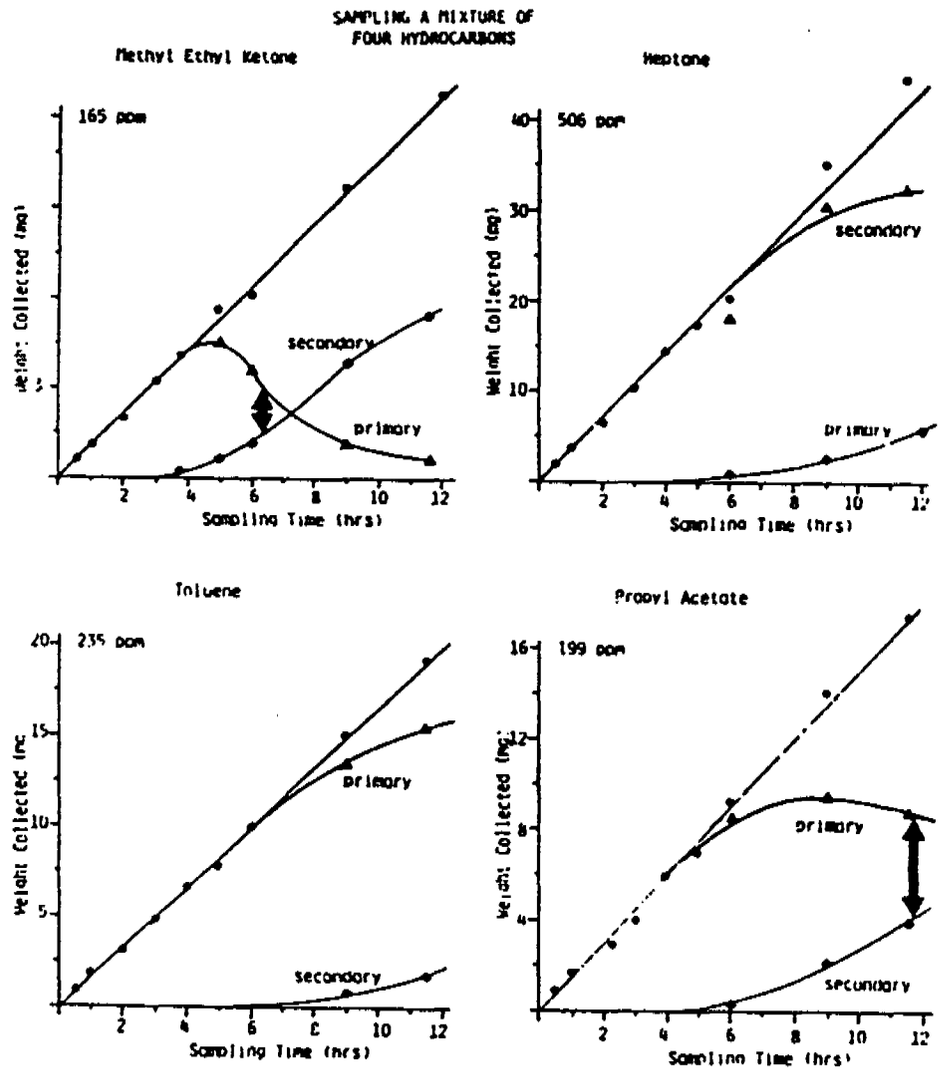
In Figure 23, at even higher concentrations, the weight ratio criteria for validity indicated that for four of the contaminants, the sampling could not be done for a 12 hour period. However, the response of the 3520 OVM as measured by the combined weight gave a linear response over the 12 hour sampling period for all contaminants except for methylene chloride. For methylene chloride, the combined weight deviates from a linear response after six hours of sampling. At this point even the secondary adsorbent is not able to properly sample methylene chloride due to the large amount of the other contaminants also being collected on the secondary adsorbent. It is again important to indicate that even though both the primary and secondary combined were not able to accurately measure the methylene chloride concentration, the sample is valid for the other contaminants even past an eight hour sampling period.

FIGURE 23



The final challenge us d to evaluate the 3520 OVM preformance was mixture of contaminants selected from different hydrocarbon families. In Figure 24, it can again be observed that the 3520 response as measured by the combined weight was a linear function of the sampling time. When sampling this mixture, it can be observed that methyl ethyl ketone was displaced from the primary adsorbent. Even with this displacement, the weight ratio criteria indicated a valid sample could be collected for a six hour sampling period and from the linear response of the combined weight a valid sample was actually collected for the entire 12 hour sampling period.

FIGURE 24



In conclusion, the above documentation of the sampling performance of the 3520 Organic Vapor Monitor with the backup section demonstrates the accuracy and validity of the samples collected from known challenges. These challenges consisted of single contaminants for which the activated carbon has limited capacity as well as mixtures with numerous components. The 3520 OVM with the secondary adsorbent has been shown to have increased effective sampling capacity as well as the ability to determine sample validity long before the combined weight deviates from the expected linear response. This assures the industrial hygienist that accurate samples will be collected under any sampling condition when the weight ratio criteria is used to determine sample validity.

Occupational Health and Safety Products Division/3M
220-7W 3M Center
St. Paul, Minnesota 55144

TECHNICAL DATA BULLETIN
104
(replaces tech data bulletin #71)

Sampling for Methylene Chloride Using the 3M 3520/3530 Organic Vapor Monitor

March 23, 1992

INTRODUCTION

OSHA has proposed that the permissible exposure limit (PEL) for methylene chloride be changed from 500 ppm to 25 ppm with an action level of 12.5 ppm and a provision for a short term exposure limit (STEL) of 125 ppm. This Technical Data Bulletin describes sampling for methylene chloride using the 3520/3530 organic vapor monitor.

SAMPLING PROCEDURE

No special techniques are required. Follow the instructions for sampling found in either the monitor sampling guide or in the instructions accompanying the monitors.

SAMPLING CRITERIA

The monitor must be exposed for at least 15 minutes and not longer than four hours. Monitoring times greater than four hours are not recommended.

The quantity of methylene chloride on the back section of the monitor must not exceed 50% of the methylene chloride found on the front section of th monitor. If the quantity of methylene chloride on the back section of the monitor is greater than 50% of the methylene chloride found on the front section of the monitor, the monitor limitation for a specific situation may have been exceeded.

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St. Paul, MN 55144-1000

In cases where complex mixtures, such as stoddard solvent or petroleum distillates, are present at a relative humidity greater than 70%, the sampling time may need to be reduced.

ACCURACY

The monitors are accurate to within +/- 25% when all sampling criteria are met.

RANGE

The minimum detectable amount of methylene chloride accurately measurable on the monitor in the 3M OH&ESD laboratory is 10 micrograms.

MINIMUM CONCENTRATION MEASUREMENTS

15 minutes.....5.1 PPM
240 minutes.....0.32 ppm

The maximum amount of methylene chloride the monitor will collect is 3000 micrograms.

MAXIMUM CONCENTRATION MEASUREMENTS

15 minutes.....1518 ppm
240 minutes.....120 ppm

Higher measurements may be possible, however the accuracy of measurements at very high levels may be less than +/- 25%.

ANALYSIS

Analysis of monitors exposed to methylene chloride is conducted following the procedures outlined in the 3M Analysis Guide. Carbon disulfide is used as the desorption solvent. The 3M OH&ESD laboratory recovery is listed as 90%. The experimentally validated sampling rate is 37.9 cc/min.

Occupational Health and
Safety Products Division/3M

3M Center
St. Paul, Minnesota 55144
612/733 1110

3M

Dear Customer:

Many industrial firms and government agencies from around the world have been conducting evaluations of the 3M Brand Organic Vapor Monitor #3500. The Occupational Health and Safety Products Division of 3M has made a concerted effort to collect and evaluate as much of this data as possible, for our information as well as that of our customer

We are pleased to be able to share with you this collection of field and laboratory information. The data has been summarized for you. It is generally divided into two categories: field tests and laboratory tests. This new section of information can be added to your 3M Brand Organic Vapor Monitor #3500 3-ring notebook.

Much of the data is submitted to 3M for anonymous publication. Many of these reports represent very thorough research on a specific organic vapor in a laboratory test. Other evaluations are in-depth field studies conducted under close supervision.

In addition to the data summaries, two complete technical papers are enclosed for your reference file; (1) The "Comparison of 3M Organic Vapor Monitor Versus Charcoal Tubes" was submitted to 3M for our use as an anonymous publication. (2) The "Evaluation of a passive dosimeter for collection of 2-bromo-2-chloro-1,1,1-trifluoroethane and 2-chloro-1,1,2-trifluoroethyl difluoromethyl ether in hospital operating rooms" by John Mazur et. al. was recently published in the May 1980 issue of the AIHA.

3M plans to be adding to this 3500 Organic Vapor Monitor notebook of information periodically with updates of new field and laboratory data as well as new Compound Sampling Rates. To insure receipt of this information, please be sure we have your correct address and spelling of your name. If you need to change the mailing address, please note the change on the enclosed blue and white reply card.

If you wish to discuss any of the enclosed information in more detail, please feel free to contact your local 3M sales representative or Occupational Health and Safety Products Technical Service on our toll free number. You may reach the proper contact by calling 800-328-1300 (in Minnesota, 612-733-8029), and asking for Occupational Health and Safety Products Customer Service.

Sincerely,

Miriam I. Merino

Miriam I. Merino
Market Coordinator
Occupational Health & Safety Products Division/3M
220-7W 3M Center
St. Paul, MN 55144

MIM:kms
9/1/80

3500 LABORATORY & FIELD TEST EVALUATIONS

TABLE OF CONTENTS

I. Laboratory Evaluations

	Compound(s)	Evaluator	Summary
a.	Toluene	Kitazato University, Japan	Four levels from 10-200 ppm were generated in a test chamber and monitors exposed to these concentrations over varying time intervals.
b.	Toluene and Toluene mixture with Iso Butanol, Acetone, and Perchloroethylene	Technical Research Center of Finland	The Center ran controlled laboratory comparisons of the #3500 vs. standard charcoal tubes and low flow pumps. The compounds studied were Toluene, a mixture of Toluene and Iso Butyl Alcohol, Acetone, and Perchloroethylene. Chamber concentrations were checked by Micron IA infrared and by direct GC analysis.
c.	Styrene/Acetone mixture	Jutlandish Institute of Technology, Denmark	The Jutlandish Institute of Technology in Denmark performed a laboratory comparison of a Styrene and Acetone mixture using #3500 OVM and SKC standard charcoal tubes. Low flow pumps were used for the SKC tubes and both systems were exposed for four hours.
d.	Vinyl Chloride	Chemical Company (anonymous)	An airstream containing 0.61 ppm of VC was passed over the #3500 for fifteen minutes at two liters per minute. Relative Precision at 95% confidence level was 15% for the #3500 and 114% for the tube.
e.	Dichloromethane, 1, 2 Dichloroethane, Tetrachloroethylene, Heptane	3M OH & SP Division	Data show that the #3500 is gas tight. This data is valid in its conclusions only when the compound is stable. The data relates storage time to recovery coefficients (Desorption Efficiency).
f.	Enflurane		A study at an eastern U.S. university was carried out comparing the #3500, Miran IA, and Charcoal Tube (C.T.) to a known concentration in an exposure chamber. The #3500 correlated well with the tank concentration and had excellent coefficient of variance.

II. Field Evaluations

	Compound(s)	Evaluator	
a.	Complex Mixtures Ketones and Chlorinated Hydrocarbons	Chemical Company (anonymous)	A field comparison was conducted between a 600 mg. charcoal tube and the #3500 in a complex mixture. Agreement is good for all cases except acetone, where it appears the #3500 samples are high. An explanation is given.
b.	Benzene, Toluene Xylene in complex mixtures	Oil Company (anonymous)	A major oil company ran extensive side-by-side comparative studies of standard charcoal tubes and the #3500. Thirty samples were taken for Benzene, Toluene, and Xylene. These compounds were present together in a complex mixture of hydrocarbons.
c.	Benzene, Toluene	Chemical Company (anonymous)	A U.S. chemical company ran side-by-side personal exposures with the #3500 and standard charcoal tubes. Benzene and Toluene were both present in the air.
d.	1, 1, 2 Trichloroethylene	3M Industrial Hygiene Department	Personal samples were run in a 3M plant. Samples were run for four hours and converted to TLV-TWA. Correlation was good between the two methods.
e.	Acetone	Chemical Company (anonymous)	Three separate methods of measuring acetone in a field area sample were used. The 600 mg. tubes were used in series to be certain that loss through the tube was minimized. Comparability between methods is good.
f.	Benzene	Steel Company (anonymous)	A U.S. company ran side-by-side area samples between the #3500 and a standard charcoal tube. The range of concentrations found were from non-detectable to over 90 ppm, with an average of 7.89 ppm. A high degree of correlation exists between the 79 pairs of sample data.

III. Lab/Field Evaluations

	Compound(s)	Evaluator	
a.	Halothane Enflurane	U. S. Army Environmental Hygiene Agency	Laboratory and field testing was performed on the subject gases. Field data was taken in both unoccupied and occupied operating rooms.
b.	Methyl Methacrylate	Chemical Company (anonymous)	Known quantities of MMA were generated in a laboratory chamber. Lab precision tests are shown, plus the side-by-side comparison of standard charcoal tube vs. the #3500 in personal field samples.

Op rationally, passiv dosimeters are ideally suited for monitoring organic vapors in hospital operating rooms as they are compact, lightweight and do not require tubing or pumps. In this study, a recently developed passive diffusion sampler was us d to collect 2-bromo-2-chloro-1,1,1-trifluoro thane (Halothane) and 2-chloro-1,1,2-trifluoroethyl difluoromethyl ether (Enflurane) in standard air mixtures over the range of 0.2 - 10 ppm. Additionally, exposures to known concentrations were conducted for various lengths of time. A side-by-side comparison of charcoal tubes (CT) and passive dosimeter collection characteristics were made on known air mixtur s and samples collected in operating rooms. The material adsorbed on charcoal from dosimet rs and CT was desorbed with carbon disulfide and quantified using gas-liquid chromatography. The overall efficiency of the dosimeters along with quality control data are presented.

Evaluation of a passive dosimeter for collection of 2-bromo-2-chloro-1,1,1-trifluoroethane and 2-chloro-1,1,2-trifluoroethyl difluoromethyl ether in hospital operating rooms

J. F. MAZUR, G. E. PODOLAK, G. G. ESPOSITO, D. S. RINEHART and R. E. GLENN
US Army Environmental Hygiene Agency, Aberdeen Proving Ground, MD 21010

introduction

It was almost a hundred years after the first use of an inhalation anesthetic in 1842 before anesthesiologists recognized the possible deleterious effects of occupational exposure to anesthetic gases. However, it has only been during the past decade that considerable effort has been directed toward the determination of trace concentrations of anesthetic gases and vapors in the operating room atmosphere, and the related potential hazards to chronically exposed personnel.

In 1974, the American Society of Anesthesiologists Ad Hoc Committee on the Effects of Trace Anesthetics published a report on a national survey conducted on occupationally related diseases among dental and operating room personnel.[1,2] At the time of this study, the number of operating room, dental, and veterinary personnel who were potentially exposed to anesthetic gases exceeded 200 000 persons per year. The results of this study, and others both human and animal, suggest that chronic exposure to anesthetic gases increases the risk of spontaneous abortion and congenital abnormalities in children of both female workers and wives of male workers. Chronically exposed personnel also showed increased incidence of hepatic and renal diseases. Other studies have indicated an increased risk of cancer and possible impairment of certain psychologic functions. Acute exposures to anesthetic gases have been shown to affect the central nervous system with resulting symptoms of headaches, nausea, fatigue, etc.[3]

For reasons of both efficacy and safety, most of the anesthetic agents introduced prior to 1950 have been replaced. The flammable and explosive inhalation anesthetic agents such as diethyl ether and cyclopropane have been replaced by nonexplosive, nonflammable anesthetics such as halothane, enflurane, and methoxyflurane. Halothane and enflurane are currently the two most widely used halogenated anesthetic agents in US Army hospitals. They are generally used in conjunction with nitrous oxide and/or intravenously injected anesthetics.

The US Army Environmental Hygiene Agency (USAEHA) is responsible for monitoring potential problem areas of occupational hazards and safety in US Army hospitals and clinics. Part of this surveillance program is concerned with operating room engineering controls and work practices affecting personnel exposure to waste anesthetic gases. Waste inhalation anesthetic gases are those gases and volatile liquids which are inadvertently released into work areas either by faulty equipment or improper work practices. Scavenging systems designed to collect waste anesthetic gases and vapors from the breathing system at the point of discharge and disposing of them outside of the operating room are the primary means of controlling waste anesthetic gases. Sufficient ventilation rates within the operating room are necessary to dilute anesthetic agents that are not captured by the scavenging system. Failure to control properly one or more of the above-mentioned sources of waste anesthetic gases can result in potentially hazardous exposures to operating room personnel. Consequently, personal and general area monitoring of operating rooms are conducted by USAEHA to determine if a health hazard exists and to pinpoint sources of exposure, whether they be defective equipment, inadequate scavenging systems, poor ventilation, or improper administration of anesthetics. After identifying the cause

The opinions or assertions contained herein are the private views of the authors and are not to be construed as reflecting the views of the Department of the Army or the Department of Defense.

and extent of exposure, recommendations are made for improving work practices and engineering controls to meet the recommended levels for occupational exposure published by the National Institute for Occupational Safety and Health (NIOSH).

At present, a safe level of exposure for waste anesthetic gas has not been established by NIOSH; instead, it recommends that exposures be suppressed to the greatest extent possible to minimize risk to operating room personnel. When used alone, NIOSH recommends occupational exposure to halothane and enflurane be controlled so that no worker is exposed at concentrations greater than 2 ppm. For halothane and enflurane their weights corresponding to 2 ppm would be 16.15 mg/cu m and 15.10 mg/cu m, respectively. These concentrations are based on a 45-liter charcoal tube sample taken over a time period not exceeding 1 hour. When halogenated agents are used in combination with nitrous oxide, levels of approximately 0.5 ppm are achievable, provided the time weighted average of nitrous oxide is controlled at the recommended 25 ppm level.

The NIOSH criteria document, "Occupational Exposure to Waste Anesthetic Gases and Vapors,"[3] provides a comprehensive review of sampling methods, analytical procedures, and real-time monitors. Typical collection methods cited in the literature include those utilizing gas syringes,[4-7] plastic sample bags,[8] and charcoal tubes.[9] These procedures make use of gas chromatography (GC) for the analysis of isolated samples. Additional analytical methods for anesthetic gases[10-15] based on GC, infrared spectroscopy (IR), and gas chromatography and mass spectrometry (GC-MS) have also been described in the literature. The forenoted procedures have proved adequate for in-depth investigations and have been used extensively in research studies. For the purpose of routine personal monitoring however, these procedures have certain shortcomings. Some of the problems relate to equipment complexity, sample collection, and sample manipulation.

Because of the unique working conditions that exist in operating rooms, it is essential that a personal sampler for monitoring worker occupational exposure meet certain performance criteria. Foremost, the collection of samples must not interfere with any of the various tasks performed by operating room personnel. In addition, areas designated as sterile zones must not be contaminated. Finally, the air sample should be proportional to a time-weighted average of anesthetic agent concentration.

Traditionally, organic vapors have been collected and concentrated using the charcoal tube (CT) technique. This method consists of pumping a known volume of air through a tube packed with charcoal for a definite period of time. Organic vapors are adsorbed onto the charcoal and subsequently desorbed with an appropriate solvent. The desorbent is analyzed with a gas chromatograph.

An alternative approach to sampling organic vapors is through consideration of fundamental molecular diffusion dosimetry. Devices based on this principle have recently found their way into the industrial hygiene marketplace, and have been used selectively for the collection of certain organic vapors. With this type of sampler, volatile compounds enter the sampler by molecular diffusion such that the rate of sample collection is a function of the organic vapor concentration in air. Since the vapors enter the dosimeter by nonmechanical means, it requires neither calibration nor electrical power.

The purpose of this investigation was to determine the suitability of the 3M Organic Vapor Monitor (OVM) for the collection of halothane and enflurane in operating room environments. Side-by-side collection of known concentrations of halothane and enflurane were conducted with OVM and CT samplers for comparison and correlation of test data. Variables studied were sampling time, sample concentration, and storage stability. In addition to the laboratory tests, samples were collected in operating rooms during administration of anesthesia to patients undergoing surgery. The effects of humidity and temperature on collection efficiency were not included in this study, since these parameters are carefully regulated in operating rooms.

experimental

passive dosimeter

All passive dosimeter monitoring was conducted with the 3M Brand Model 3500 Organic Vapor Monitor (OVM), 3M Company, St. Paul, MN. This unit consists of a round nylon body approximately 4.5 cm in diameter, weighing about 12 grams. A charcoal adsorbent pad is located inside the monitor, separated by spacers from a diffusion membrane. Contaminants enter the monitor by molecular diffusion and are adsorbed onto the charcoal. At the conclusion of the sampling period, the diffusion membrane is removed, and a tight-fitting cap firmly snapped into place. The cap contains two ports which are sealed by inserting the attached plugs. When the sample is ready for chromatographic analysis, the center port is opened and 1.5 mL of carbon disulfide is introduced into the monitor via a glass syringe. The center port is resealed, and the sample is allowed to desorb for 30 minutes. A GC sample is taken directly from the center port with a 10-μL syringe. The OVM sampler and cover are shown in Figure 1.

The time-weighted worker exposure level is calculated using the following equations:

$$\text{mg/m}^3 = \frac{\text{Corrected weight on badge (nanograms)}}{\text{Sampling rate (cm}^3\text{/min)} \times \text{Sampling time (min)}}$$

$$\text{ppm} = \frac{\text{mg}}{\text{m}^3} \times \frac{22.4\ \text{L/mole}}{\text{mwg/mole}} \times \frac{T°\text{K}}{273°\text{K}} \times \frac{760\text{-mm Hg}}{\text{P-mm Hg}}$$

The sampling rates for halothane and enflurane are 25.1 cm^3/min and 26.9 cm^3/min, respectively. These sampling rates were calculated from diffusion coefficients corresponding to each compound.

charcoal tube monitor

Charcoal tubes containing two sections of charcoal, 200/400 mg, were purchased from SKC Inc., Eighty Four, PA. Samples were collected at two different sampling rates, 30 mL/min (Accuhaler 808, Lefco Engineering) and 500

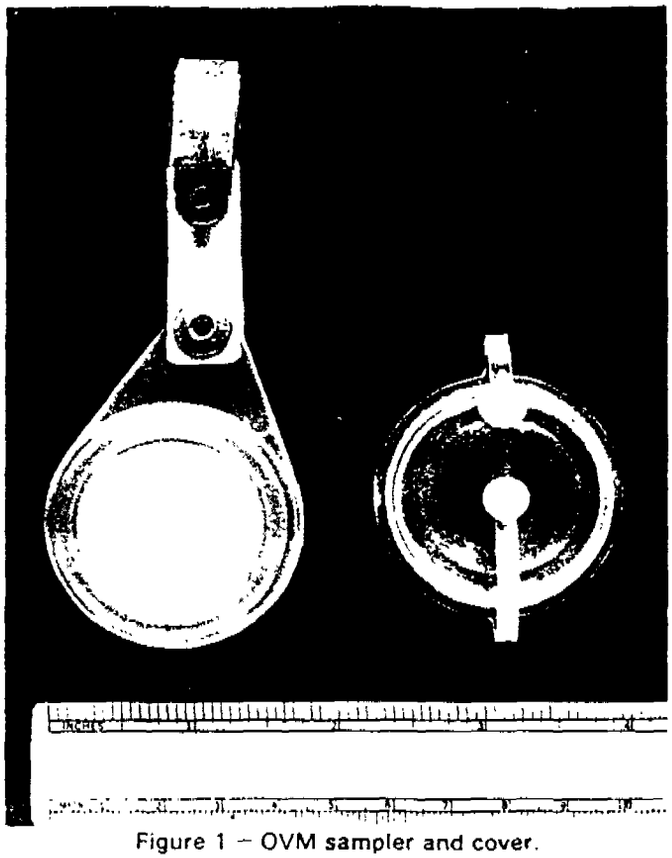

Figure 1 – OVM sampler and cover.

mL/min (Model P-4000A, E. I. du Pont de Nemours & Co., Wilmington, DE). Pump calibration was accomplished by connecting a charcoal tube to a pump and measuring the air flow with a bubble meter. When the sample was ready for chromatographic analysis, the charcoal was poured from the glass sampling tube into a 10-mL vial and desorbed with 2 mL of carbon disulfide.

gas chromatography

Analysis of desorbent solutions was performed on a Hewlett-Packard Model 5830 gas chromatograph equipped with a flame ionization detector and HP 18850A GC Terminal. The GC operating conditions were as follows: column, 17 ft. × 1/8 in. stainless steel packed with 30% Apeizon L on 80-100 mesh Chromosorb W-HP; injection port temperature, 130° C; detector temperature, 300° C; initial column temperature, 120° C; final column temperature, 190° C; column temperature programming rate, 30°/min.

test atmosphere

Appropriate amounts of halothane and enflurane were injected into a 2-mL vial equipped with a septum and screw cap. The vial was transferred to a 6920-liter static test chamber and positioned in front of a circulating fan. The vial cap was removed and the chamber door closed immediately. After sealing the door, the circulating fan was turned on and 30 minutes were allowed to elapse to insure complete mixing of the anesthetic agents with air. The OVM's were attached to a meter stick and inserted into the chamber through a side-access port. CT samples were collected at a port adjacent to the OVM's. For some experiments having short sample collection times, successive tests were conducted using the same chamber concentration.

results and discussion

OVM and CT data for various concentrations of halothane and enflurane are presented in Table I. Test atmospheres for Samples 1-3 contained only halothane, whereas test Samples 4-8 were binary mixtures of both halothane and enflurane. The sampling rate for Samples 6 and 7 was 30 mL/min; the sampling rate for all other samples was 500 mL/min. In general, results from the OVM's were in good agreement with the theoretical values; whereas, results from the CT's showed a slight positive bias. Statistical treatment of the OVM data is presented in Table II.

The values shown in Table II were derived from four replicates for each test. Since the GC analysis is an integral part of each test, the statistical data reflect the overall efficiency of both sample collection and analytical procedures. In general, the precision and accuracy were within acceptable limits over the tested concentration range. In summary, a total of 44 OVM's were tested for halothane, and 25 OVM's for enflurane, at four concentration levels (0.5, 2, 5, and 10 ppm). An overall recovery of 100.6% and a

TABLE I
Halothane and Enflurane Laboratory Data

Sample	Exposure Time OVM, Hrs	Theoretical Conc., ppm	Mean Observed Enflurene, ppm OVM[A]	CT[B]	Mean Observed Halothane, ppm OVM[A]	CT[B]
1	4	5	--	--	5.28	5.14
2	2	5	--	--	5.34	5.40
3	4	2	--	--	2.13	2.23
4	4	0.5	0.57	0.64	0.48	0.59
5	4	2	1.95	2.13	2.27	2.30
6	2	2	1.65	2.47	2.06	2.22
7	1	2	2.01	2.11	1.95	2.11
8	4	10	9.17	11.49	9.51	10.30

[A]Average of four OVM's.

[B]Average of two CT s for Samples 6 and 7; all others average of four CT's.

TABLE II
Statistical Summary of OVM Results

Exposure Time Hrs	Theoretical Concentration ppm	Halothane Mean Recovery %	Halothane RSD %	Enflurane Mean Recovery %	Enflurane RSD %
4	0.5	96.0	4.7	114.0	3.1
1	2.0	97.5	6.7	100.5	10.1
2	2.0	103.0	14.1	82.5	1.7
4	2.0	106.5	15.4	--	--
4	2.0	113.5	2.5	97.5	0.8
4	5.0	105.6	4.0	--	--
2	5.0	106.8	5.4	--	--
4	10.0	95.1	2.0	91.7	1.9

relative standard deviation (RSD) of 5.6% for halothane, and 96.5% recovery and an RSD of 3.5% for enflurane were observed.

In order to determine the storage stability of halothane, two sets of four OVM's were exposed at the same time for 1 hour in the static test chamber; one set was analyzed within 24 hours, and the other set was stored at room temperature for 2 weeks before GC analysis was performed. No special precautions were taken; nor were the monitors stored in the foil envelopes. The test was repeated for halothane and enflurane (Sample 2) with the storage time extended to 3 weeks. Again, no special storage precautions were taken. As shown in Table III, there was no significant loss of analyte when OVM's were stored up to 3 weeks. It should be noted, however, that the results from Sample 2 were somewhat higher after storage. Since an actual increase during storage is not possible, this variance was attributed to the imprecision of the analytical procedure and not the fault of the sampling technique. Similar tests (Samples 3 and 4) were conducted on enflurane and halothane at concentrations near the detection limit of the method. Loss of analyte during storage was not observed.

Table IV provides comparative field data of samples obtained during simulated and actual surgery. In tests 1-3, halothane and nitrous oxide were leaked into an unoccupied operating room equipped with a scavenging system; nitrous oxide was added at a rate equivalent to amounts commonly used with halothane. In order to achieve simultaneous and uniform sampling of the operating room atmosphere, OVM's and CT's were positioned on top of an IR analyzer located between the anesthetic gas source and the wall mounted exhaust register. A good correlation was observed between OVM, CT, and IR monitors. Of special significance is the excellent agreement among results obtained on Sample 1. Although an agreement between the OVM, CT, and IR results for Sample 2 is not quite as good, it should be noted that the OVM result falls between CT and IR. Samples 4, 5, and 6 represent multipoint collections of samples taken during surgery, the anesthesia being used was nitrous oxide and enflurane. As not to interfere with any of the operating room practices, the sampling apparatus for Sample 4 was located along the wall furthest removed from the surgical team. Also, in keeping with previously conducted tests, OVM's and CT's were placed in close proximity to each other. The enflurane concentration level obtained with these samplers is shown in Table IV. Other OVM's (Sample 5) were placed on top of the anesthetic gas machine. As expected, this concentration was significantly higher than the level found in Sample 4 where enflurane had the opportunity to diffuse and become more dilute. The OVM for Sample 6 was attached to the collar of the anesthesiologist prior to surgery and removed in the recovery room after surgery. The overall exposure time was 2 hours and 5 minutes, and corresponding time-weighted average for enflurane was 0.58 ppm.

conclusion

The results presented in this study indicate the OVM to be a reliable, convenient method for collection of enflurane and halothane in operating room environments. Moreover, it offers several advantages over pump-type monitors. The OVM is small and compact and, because of its simplistic design, is not subject to malfunction. In addition, passive

TABLE III
OVM Storage Stability

Sample	Storage Time	Halothane, ppm Before Storage	Halothane, ppm After Storage	Enflurane, ppm Before Storage	Enflurane, ppm After Storage
1	2 wks	1.95	1.83	--	--
2	3 wks	1.92	2.09	1.66	1.75
3	2 wks	0.17	0.16	0.19	0.17
4	3 wks	0.18	0.15	0.19	0.19

TABLE IV
Field Data

Sample	Halothane OVM ppm[A]	Halothane CT ppm[B]	Halothane IR ppm[C]	Enflurane OVM ppm[A]	Enflurane CT ppm[B]
1	3.42	3.43	3.53	--	--
2	1.87	2.04	1.78	--	--
3	0.40	0.56	0.55	--	--
4	--	--	--	0.49	0.52
5	--	--	--	1.39	(N)
6	--	--	--	0.58	(N)

[A]Average of four OVM's.

[B]Average of two CT's.

[C]Integration of chart reading

(N)Not taken so as to not interfere with operating room procedures.

dosimeters come preassembled, whereas CT dosimeters require on-site assembly of components. Most important, utilization of the OVM does not interfere with personnel work routines nor present a contamination problem. Finally, the OVM becomes cost-effective when one takes into account equipment costs and personnel time required for the operation and maintenance of a charcoal tube sampling system.

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AWS Safety/Health research program fund drive

The American Welding Society has launched a major fund drive to support a Welding Safety and Health Research Program with the overall objectives of: 1) demonstrating that the welding environment can be safe when responsible environmental precautions are followed and 2) meeting government requirements, that are technically and economically feasible.

One long range research project will be concerned with the health effects of the welding environment on those who work with mild steel. Other research projects that are planned include a detailed chemical analysis of welding fume, a design for optimum ventilation systems, and short and long-term animal testing to predict health effects. Safety training materials will be developed as part of this Research Program.

All companies and organizations within the welding industry, as well as all those with a vested concern for advancements in the fields of occupational safety and health, are being asked to financially support this Research Program to a reasonable degree — consistent with the importance of welding within the individual company or organization structure.

To fund the projects now ready for implementation, a minimum of $500,000 is required per year for the next five to ten years.

A brochure "Creating a Healthful Environment . . . a Challenge to the Welding Industry" containing additional details on this Program, is available from Publications Services, American Welding Society, 2501 N.W. 7th Street, Miami, FL 33125. Telephone 305/642-7090. For additional information on this Program, contact Marvin Kennebeck, AWS Safety and Health Manager, at the American Welding Society.

I. #3500 LABORATORY EVALUATION

A. Toluene

Dr. T. Takada of Kitazato University in Japan studies the response of the #3500 to varying time-concentration relationships of toluene. Four levels from 10-200 ppm were generated in a test chamber. Monitors were exposed to these concentrations over varying time intervals. Temperature and humidity were kept constant at 24.3 C and 51%.

Results show that the monitors can accurately predict varying concentration over time.

A fifteen minute side-by-side exposure with charcoal tubes also shows excellent agreement.

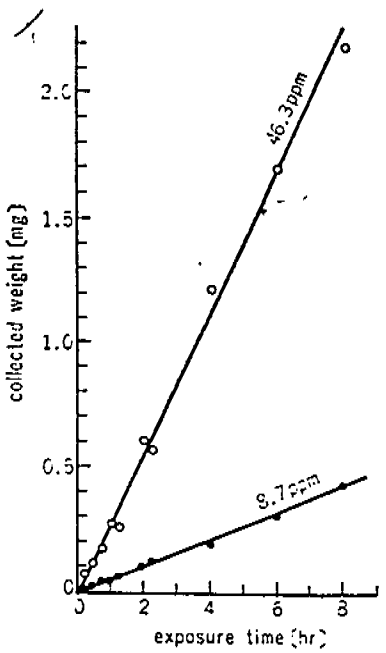


図 2 Relation between exposure time and weight of Toluene collected in 3M organic vapor monitor

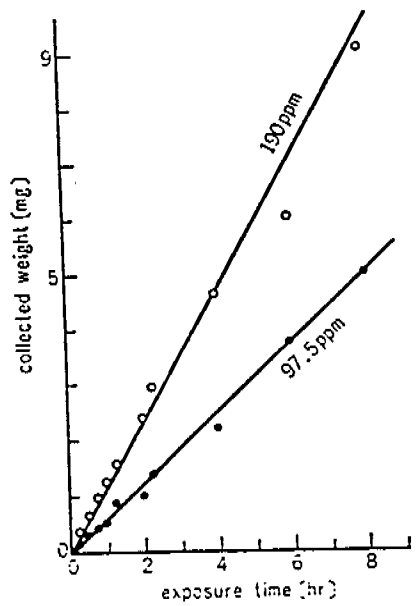


図 3 Relation between exposure time and weight of Toluene collected in 3M organic vapor monitor

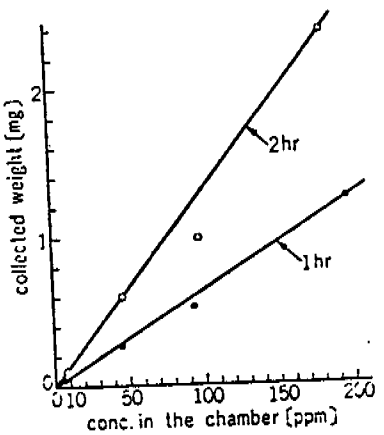


図 4 Relation between concentration in chamber and collected weight of Toluene in 3M organic vapor monitor

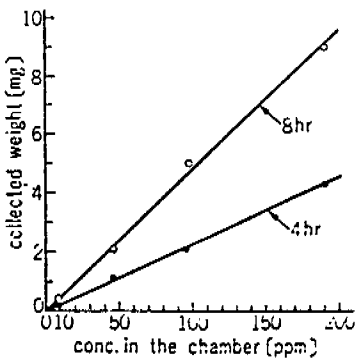


図 5 Relation between concentration in chamber and collected weight of Toluene in 3M organic vapor monitor

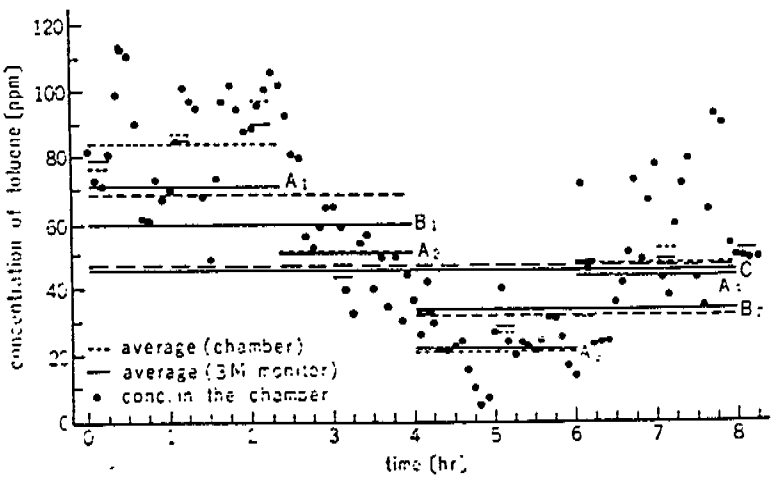


図 7 Temporal change of Toluene concentration in chamber and TWA concentration by 3M monitor

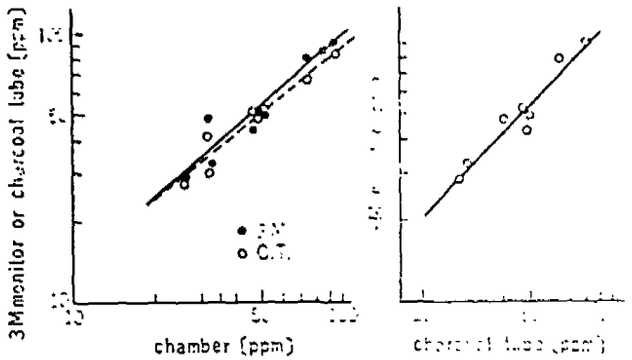


図 8 Relation between Toluene concentration by 3M monitor and by charcoal tube and the one in the chamber

表 2 Monitor and chamber concentration and collection rate of Toluene vapor

exposure time	monitor conc. (ppm)	chamber conc. (ppm)	collection (rate%)
0 —0 : 15	78.8	76.1	103.5
0 : 00—1 : 15	84.5	86.7	97.5
2 : 00—2 : 15	90.1	97.1	92.8
3 : 00—3 : 15	43.2	46.9	92.1
4 : 00—4 : 15	32.6	32.7	99.7
5 : 00—5 : 15	28.6	26.5	107.9
6 : 00—6 : 15	47.7	31.7	150.5
7 : 00—7 : 15	48.7	52.1	93.5
8 : 00—8 : 15	51.7	49.2	105.1
0 —2 : 20	70.7	83.8	84.4
2 : 20—4 : 00	50.9	51.1	98.8
4 : 00—6 : 00	21.6	20.6	104.9
6 : 00—8 : 00	43.7	47.6	91.8
0 —4 : 00	59.1	68.5	86.3
4 : 00—8 : 00	33.6	31.8	105.7
0 —8 : 00	45.3	46.8	96.8

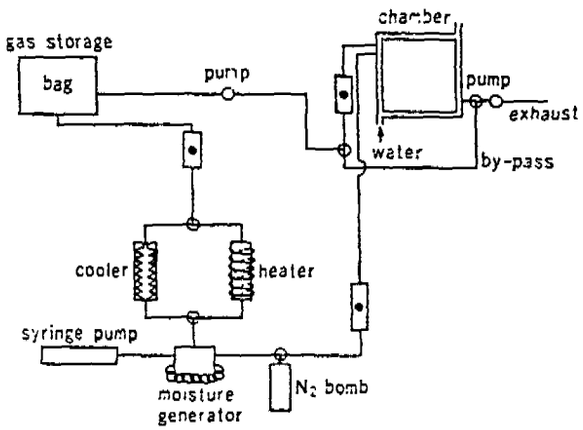


図 6 Schematic diagram of experimental apparatus

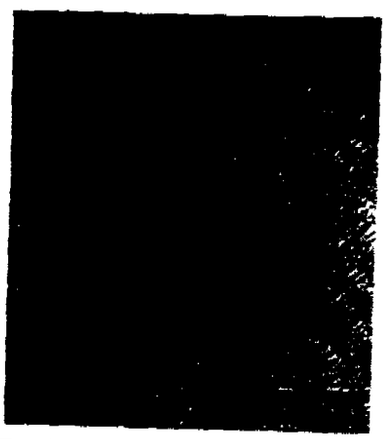


写真 2 Scanning electron microscopic photograph of white membrane

写真 3 Scanning electron microscopic photograph of active adsorbent medium

II. #3500 LABORATORY EVALUATION

B. Toluene and mixture of Toluene, Isobutyl Alcohol, Acetone, and Perchloroethylene.

The Technical Research Center of Finland ran controlled laboratory comparisons of the #3500 vs. standard charcoal tubes and calibrated, low flow pumps. The compounds studied were Toluene, a mixture of Toluene and Iso Butyl Alcohol, Acetone, and Perchloroethylene. Chamber concentrations were checked by Miran IA infrared and by direct GC analysis.

Agreement with the reference methods are excellent except in the case where exposure time was less than the recommended fifteen minutes or deliberate overload conditions were chosen. In Overload conditions, the 3500 more closely estimated the concentration than the tube.

TOLUENE

TECH. RESEARCH CENTER OF FINLAND

SAMPLE TIME - 4 hrs.

RESULTS - PPM

	TEST #1	TEST # 2
MIRAN, IA	288	89
GC	289	86
3500 #1	297	86
#2	287	87
#3	-	87
#4	-	85
#5	-	88
#6	-	88
#7	-	87
#8	-	89
TUBE #1	283	85
TUBE #2	-	85

TOLUENE

TECH RESEARCH CENTER OF FINLAND

RESULTS - PPM

SHORT TERM SAMPLING

	Test #1	Test #2	Test #3
Sample Time (min.)	20	15	10
Miran, IA	560	560	560
GC	544	544	544
#3500 #1	550	600	503
#3500 #2	542	530	529

MIXTURE TEST

TECHNICAL RESEARCH CENTER OF FINLAND

MONITOR - 3M #3500

RESULTS - PPM

SAMPLE TIME:

TUBES 1 & 2 - 66 min.

TUBES 3 & 4 - 30 min.

#3500 - 220 min.

	ISO BUTYL ALCOHOL	TOLUENE
Miran, IA	144	180
G. C.	143	175
Tube 1	150	164
Tube 2	138	168
Tube 3	138	169
Tube 4	130	169
#3500 1	138	166
2	148	178
3	144	176
4	142	165
5	146	180
6	144	170
Tube	139 $\pm$ 8.2	168 $\pm$ 2.4
#3500	144 $\pm$ 3.5	173 $\pm$ 6.4

ACETONE

TECH RESEARCH CENTER OF FINLAND

RESULTS - PPM

	Test #1	Test #2*	Test #3
Sample time (min.)	65	240	240
Miran, IA	1070	1555	385
GC #1	1066	1538	380
GC #2	-	1560	-
#3500 #1	1043	1338	373
#3500 #2	1063	1210	400
Tube #1	-	1018	377
Tube #2	-	1007	400

*Deliberate Overload Condition

PERCHLOROETHYLENE

TECH RESEARCH CENTER OF FINLAND

SAMPLE TIME - 4 hrs.

RESULTS - PPM

	TEST #1	TEST #2
Miran, IA	120	42
GC #1	121	40
GC #2	125	42
#3500 #1	124	41
#3500 #2	121	42
Tube	122	-

I. #3500 LABORATORY EVALUATION

C. Styrene and Acetone Mixture

The Jutlandish Institute of Technology in Denmark performed a laboratory comparison of a Styrene and Acetone mixture using #3500 OVM and SKC standard charcoal tubes. Low flow, calibrated pumps were used for the SKC tubes and both systems were exposed for four hours. Two separate tests were conducted at different concentrations of the Acetone - Styrene mixture. Comparability of the two methods for the mixture is demonstrated.

JUTLANDISH TECHNOLOGICAL INSTITUTE - DENMARK

MONITOR - 3M #3500

PUMP & TUBE - SKC

EXPOSURE TIME - 4 HRS.

RESULTS - Mg/M^3

TEST #1	TUBE #1	TUBE #2	MONITOR #1	MONITOR #2
Acetone	699	710	677	694
Styrene	358	344	349	378

TEST #2	TUBE #3	MONITOR #3	MONITOR #4
Acetone	198	187	192
Styrene	125	120	124

ANALYTICAL UNCERTAINTY $\leq \pm$ 5% RELATIVE

I. #3500 LABORATORY EVALUATION

D. Vinyl Chloride

A chemical company set up a lab trial to expose both #3500 and a standard charcoal tube to 0.61 ppm of VC.

An airstream containing 0.61 ppm of VC was passed over the #3500 for fifteen minutes at two liters per minute.

The same airstream was introduced into gas sampling bags and then pulled through the tube in ninety minutes with a low flow pump.

Relative Precision at 95% confidence level was 15% for the #3500 and 114% for the tube.

VINYL CHLORIDE

EXPOSURE - 0.61 PPM

RESULTS - PPM

#3500		PUMP & TUBE
0.63		2.3
0.48		1.2
0.56		0.4
0.52		0.8
0.65		0.05
0.71		
0.59	$\bar{X}$	0.95
0.09	S	0.87

I. LABORATORY EVALUATION

E. Stability of Samples using Dichloromethane, 1, 2 Dichloroethane, Tetrachloroethylene, Heptane.

The following data shows that the #3500 is gas tight. The data relate storage time to recovery coefficients (Desorption Efficiency). This data are valid only when the compound is stable.

Recovery Coefficients may drop due to decomposition, polymerization, etc. over extended storage time.

Methyl Ethyl Ketone is an example of decaying recoveries over time.

Reliability of samples are not assured if the captured volatile compound can escape during storage.

Storage Life

	Test	Days	Recovery $\pm 2\sigma$
Dichloromethane	1	1	.02 ± .02
	2	3	.93 ± .06
	3	10	.91 ± .02
	4	14	.90 ± .01
	5	31	.90 ± .01
1,2-Dichloroethane	1	1	.99 ± .01
	2	3	.98 ± .03
	3	10	.97 ± .01
	4	14	.96 ± .02
	5	31	.96 ± .01
Tetrachloroethylene	1	1	1.00 ± .05
	2	3	1.02 ± .01
	3	10	1.00 ± .08
	4	14	1.02 ± .02
	5	31	1.01 ± .03
Heptane	1	1	1.04 ± .06
	2	81	1.05 ± .02
	3	132	1.03 ± .04
	4	237	1.04 ± .03

I. #3500 LABORATORY EVALUATION

F. Enflurane

A study at an eastern U.S. university was carried out comparing the #3500, Miran 1A and Charcoal Tube (C.T.) to a known concentration in an exposure chamber. The Miran sampled continuously with readings taken at fifteen minute intervals. Velocity scans were taken along with pressure and temperature to insure uniformity of exposure conditions.

The #3500 correlated well with the tank concentration and had excellent coefficient of variance. The regression slope of #3500 versus tank concentration was 0.95.

ENFLURANCE

LABORATORY STUDY

CORRELATION COEFFICIENTS

LINEAR REGRESSION

3500 - Tank	0.960
3500 - C. T.	0.970
3500 - Miran	0.963

LINEAR REGRESSION (FIT THROUGH ZERO)

3500 - Tank	0.990
3500 - C. T.	0.993
3500 - Miran	0.990

COEFFICIENTS OF VARIATION

TANK CONC. (PPM)	3500	MIRAN	C.T.
5	0.08	0.10	0.11
10	0.06	0.07	0.27
20	0.16	0.03	0.25

ENFLURANE

LAB STUDY

RESULTS - PPM

TANK	3500	C.T.	MIRAN
5	5.6	5.2	4.4
	4.8	5.2	4.4
	4.6	4.6	4.2
	4.6	4.6	4.2
	4.6	5.0	4.2
	4.6	5.0	4.2
10	9.2	10.4	8.8
	9.7	10.4	8.8
	8.2	8.5	7.8
	9.2	8.5	7.8
	9.7	8.9	8.0
	9.7	8.9	8.0
20	19.4	19.7	15.9
	19.4	19.7	15.9
	18.1	19.3	15.3
	17.6	19.3	15.3
	19.1	20.9	15.9
	27.5	20.9	15.9
	19.1	19.2	15.9
	19.4	19.2	15.9

II. FIELD EVALUATION

A. Complex Mixtures

A U.S. chemical company ran a field comparison between a 600 mg. charcoal tube and the #3500 in a complex mixture. Agreement is good for all cases except acetone, where it appears the #3500 samples are high.

In fact, the #3500 is more closely estimating the true valve. In these conditions, it is believed that acetone is subject to displacement and is more readily swept from the tube. A diffusional system has no flow of air, only organic vapor, and suffers less from displacement losses.

MIXTURES

SAMPLE TIME: 6 hrs.

RESULTS - PPM

TUBE - 600 mg.

	#3500	Pump & Tube
MIBK	8.5	4.6
TOLUENE	16.5	13.8
N-BUTYL ACETATE	2.3	2.5
XYLENE	0.4	0.3
MEK	ND	ND
ACETONE	264	115
METHYLENE CHLORIDE	0.5	0.3
TRICHLOROETHYLENE	0.6	0.4
PERCHLOROETHYLENE	0.5	0.3
ACETONE	66.7	45.2
METHYLENE CHLORIDE	11.3	9.2
TRICHLOROETHYLENE	0.1	0.1
PERCHLOROETHYENE	0.6	0.4
ACETONE	35.4	17.0

II. FIELD EVALUATIONS

B. Field Samples of Aromatics; Benzene, Toluene, Xylene in complex mixtures.

A major oil company ran extensive side-by side comparative studies of standard charcoal tubes and the #3500. Thirty samples were taken for Benzene, Toluene and Xylene. These compounds were present together in a complex mixture of hydrocarbons.

The #3500 showed good agreement with the means and deviations generated by the tube. The methods correlate well in this field sampling of mixtures.

FIELD SAMPLES - AROMATICS

NUMBER OF SAMPLES - 30

CHARCOAL TUBE (CT.) VS. #3500

RESULTS - PPM

	MEAN	STD. DEV.
BENZENE - 3500	0.396	0.418
BENZENE - CT	0.334	0.405
TOLUENE - 3500	0.508	0.715
TOLUENE - CT	0.463	0.699
XYLENE - 3500	0.397	1.065
XYLENE - CT	0.367	0.863

CORRELATION COEFFICIENTS

Benzene - 0.894

Toluene - 0.935

Xylene - 0.966

II. FIELD EVALUATION

C. Benzene-Toluene Mixture

A U.S. chemical company ran side-by-side personal exposures with the #3500 and standard charcoal tubes. Benzene and Toluene were present at the same time in the air.

For Benzene, the correlation coefficient is 0.936 with linear regression of:

$$C.T. = 0.823\ (OVM) + 0.009$$

For Toluene, the correlation coefficient is 0.973 with linear regression of:

$$C.T. = 1.02\ (OVM) - 0.018$$

BENZENE - TOLUENE

PERSONAL SAMPLES

SAMPLE TIME: 8 hrs.

RESULTS - PPM

BENZENE		TOLUENE	
#3500	Pump & Tube	#3500	Pump & Tube
0.17	0.19	0.15	0.17
0.15	0.13	0.10	0.06
0.15	0.12	0.18	0.22
0.10	0.02	0.13	0.02
0.12	0.14	ND	ND
0.05	0.03	ND	ND
0.05	0.05	ND	ND
0.80	0.84	1.12	1.18
0.20	0.14	0.02	0.02
0.05	0.03	0.05	0.04
0.20	0.15	0.10	0.10
0.80	0.50	0.45	0.26
0.08	0.19	0.15	0.24
0.02	0.02	0.05	0.02
ND	ND	0.05	0.05

ND - Non Detected

II. FIELD EVALUATION

D. 1,1,2-Trichloroethylene

3M Company Industrial Hygiene ran comparison personal samples in a 3M plant. Samples were run for four hours and converted to TLV-TWA. Correlation was good between the two methods.

1,1,2 TRICHLOROETHYLENE

3M PLANT

SAMPLE TIME: 4 hrs.

RESULTS - PPM

CORRELATION COEFFICIENT = 0.991

#3500	PUMP & TUBE
0.8	0.8
0.7	0.6
7.3	8.5
5.1	5.9
4.2	3.9
2.2	2.0
4.0	4.6
3.4	4.9
1.0	0.9
1.4	1.1
9.8	11.9
7.6	9.6
0.4	0.2
3.0	3.4
1.6	1.8
3.1	2.8

II. FIELD EVALUATION

E. Acetone

Three separate methods of measuring acetone in a field area sample were used. The 600 mg. tubes were used in series to be certain that loss through the tube was minimized.

Comparability between methods is good.

ACETONE

AREA SAMPLES

Rh = 45% - 58%

RESULTS - PPM

METHOD #1	METHOD #2	METHOD #3
15 l Bag	2-600 mg tubes	#3500
Pump - 30 cc/min	Pump - 40-60 cc/min	Sample time:
Sample time: 3-6 hrs.	Sample time: 3-6hrs.	3-6 hrs.
182	175	194
189	-	221
354	307	331
370	323	322
419	-	456
491	484	458
152	131	135
147	116	136

II. FIELD EVALUATION

F. Benzene

A steel company ran side-by-side area samples between the #3500 and a standard charcoal tube. The range of concentrations found were non-detectable to over 90 ppm, with an average of 7.89 ppm.

A high degree of correlation exests between the 79 parts of sample data.

BENZENE

AREA SAMPLES

CHARCOAL TUBE (C.T.) vs. #3500

NUMBER OF SAMPLES - 79

CONCENTRATION RANGE - 0-90 PPM

AVG. CONCENTRATION - 7.89 PPM

REGRESSION EQUATION

#3500 = 1.063 (C.T.) + 0.091

r = 0.9988

r (Indoor) = 0.9980

r (Outdoor) = 0.9991

BENZENE PRESENT IN ATMOSPHERE CONTAINING TOLUENE AND XYLENE.

III. LABORATORY & FIELD EVALUATION

A. Enflurane and Halothane

The U.S. Army Environmental Hygiene Agency performed both laboratory and field testing on the subject gases. Field data was taken in both unoccupied and occupied operating rooms.

The statistical data is for the lab trials and shows percent of theoretical measured by the monitor. Variability is measured by relative standard deviation.

The complete study is published in the May 1980 AIHA Journal.

HALOTHANE AND ENFLURANE LABORATORY DATA

Sample	Exposure Time OVM, Hrs	Theoretical Conc., ppm	Mean Observed Enflurance, ppm OVM*	CT+	Mean Observed Halothane, ppm OVM*	CT+
1	4	5	--	--	5.28	5.14
2	2	5	--	--	5.34	5.40
3	4	2	--	--	2.13	2.23
4	4	0.5	0.57	0.64	0.48	0.59
5	4	2	1.95	2.13	2.27	2.30
6	2	2	1.65	2.47	2.06	2.22
7	1	2	2.01	2.11	1.95	2.11
8	4	10	9.17	11.49	9.51	10.30

*Average of four OVM's

+Average of two CT's for Samples 6 and 7; all others average of four CT's

Charcoal Tube - SKC 200/400 mg

Tube Sample Rates - 30 ml/min + 500 ml/min.

STATISTICAL SUMMARY OF OVM RESULTS

Exposure Time Hrs.	Theoretical Concentration ppm	Halothane Mean Recovery %	Halothane RSD %	Enflurane Mean Recovery %	Enflurane RSD %
4	0.5	96.0	4.7	114.0	3.1
1	2.0	97.5	6.7	100.5	10.1
2	2.0	103.0	14.1	82.5	1.7
4	2.0	106.5	15.4	--	--
4	2.0	113.5	2.5	97.5	0.8
4	5.0	105.6	4.0	--	--
2	5.0	106.8	5.4	--	--
4	10.0	95.1	2.0	91.7	1.9

	HALOTHANE	ENFLURANE
OVERALL RECOVERY	100.6	96.5
RELATIVE STANDARD DEVIATION (RDS)	5.6	3.5

FIELD DATA

Sample	Halothane OVM ppm*	Halothane CT ppm+	Halothane IR ppm**	Enflurane OVM ppm*	Enflurane CT+ ppm+
1	3.42	3.43	3.53	--	--
2	1.87	2.04	1.78	--	--
3	0.40	0.56	0.55	--	--
4	--	--	--	0.49	0.52
5	--	--	--	1.39	#
6	--	--	--	0.58	#

*Average of four OVM's
+Average of two CT's.
**Integration of chart reading
#Not taken so as to not interfere with operating room procedures.
Samples 1-3 & 4-5 - Area Samples
Sample 6 - Personal Sample

III. LABORATORY AND FIELD EVALUATION

B. Methyl Methacrylate

A dynamic standards generator was used to produce known quantities of MMA in a laboratory chamber. Percent relative error of the #3500 over concentrations of 8.3, 23.9, 48.3 and 92.8 PPM averaged 3.2% with a range of 0.4-4.8%.

Lab precision tests are shown, plus the side-by-side comparison of standard charcoal tubes vs. the #3500 in personal field samples.

LAB PRECISION TEST

METHYL METHACRYLATE

RESULTS - mg./hr.

SAMPLE NUMBER - 6

EXPOSURE TIME - 8 HRS.

THEORETICAL CONCENTRATION (PPM)	#3500 (mg/hr)
48.3	$\bar{x}$ = 0.3358 s = 0.0058 %CV = 1.73
23.96	$\bar{x}$ = 0.1795 s = 0.0011 %CV = 0.63
8.36	$\bar{x}$ = 0.0573 s = 0.0005 %CV = 0.95%

FIELD SAMPLES

METHYL METHACRYLATE

RESULTS - PPM

#3500	PUMP & TUBE
90.6	88.1
57.0	61.6
187.8	146.5
6.0	5.50*
2.3	3.2
4.8	6.3
35.5	38.5
3.8	4.0
2.5	2.9
2.3	2.6
5.1	5.6
3.1	2.3

*Avg. of two samples

COMPARISON OF 3M ORGANIC VAPOR MONITOR VERSUS CHARCOAL TUBES

In the Organic Vapor Monitor (OVM) only the contaminant is transported. The OVM consists of a charcoal disc of known area. A draft shield is a known distance above the disc. Between the draft shield and the disc, contaminant transport is by diffusion. The driving force is the difference between the contaminant concentration at the draft shield surface (the concentration one wishes to measure) and at the surface of the collection disc (which is essentially zero). The total amount of contaminant collected is proportional to the area of the disc, the driving force, the diffusion coefficient, and the duration of exposure, and inversely proportional to the distance between the draft shield and the disc [$N = DA/L\ (C_e - 0)\ T$]. Thus, since D, A, and L are constants, if one determines the amount collected (N) and the duration of exposure (t), the average concentration (C_e) can be calculated.

Of the seventy-nine (79) sets of paired samples, only two were personal samples. The remainder were general area samples. In all cases the opening to the charcoal tube was within approximately 1 to 2 inches of the draft shield of the OVM. All sample sets had a minimum sampling period of six hours. In some cases the total sampling period was split between two charcoal tubes, and a time-weighted average was determined. However, in the majority of the cases only one tube was used per sampling period.

Although in these field tests the samples were analyzed for benzene, toluene and xylene, the subject report is only an analysis of the benzene results. This is mainly because benzene exposure measurement is more important presently than toluene and xylene. All results in this report refer to benzene measurements. Further reports will analyze the toluene and xylene data.

Results

For the 79 sample pairs, the benzene concentrations ranged from 0.00 ppm (or non-detectable) to slightly greater than 90 ppm. Based on the charcoal tube results (using charcoal tube as the independent variable), the sample distribution is listed in Table I. A list of all the individual sample results is contained in Table III at the end of the report.

TABLE I

Concentration Range	No. of Samples	% of Total	Cumulative %
1 ppm	32	39.3	39.3
1- 5 ppm	26	32.9	72.2
5-10 ppm	8	10.1	82.3
10-25 ppm	6	7.6	89.9
25 ppm	8	10.1	100.0

Average = 7.89 ppm
Std. Dev. = 15.99 ppm

The following linear regression equation of best fit was generated from the 79 samples pairs:

OVM = 1.063 x Charcoal Tube + 0.091

The coefficient of correlation (r) for this data equals 0.9988. A r-value of 1.0 would represent a perfect correlation.

Of the 79 sample pairs, 32 were taken indoors and 47 were taken outdoors. In order to see if there were any apparent differences in the two sampling circumstances, separate analyses were also performed on each set. The following regression equations were generated:

INDOOR: OVM = 1.081 x Charcoal Tube + 0.043
r = 0.9980 n = 32 samples

OUTDOOR: OVM = 1.058 x Charcoal Tube + 0.107
r = 0.9991 n = 47 samples

In addition to the correlation field tests performed, a few precision tests on the OMV were conducted. Although 3M has conducted a great number of lab precision tests, few field tests have been conducted. A total of five sets of four OVM's were exposed. In each set two were analyzed by 3M and two by our lab. The results are listed in Table II.

TABLE II

Set 1	Set 2	Set 3	Set 4	Set 5
R-30.03	R- 1.03	R- 0.64	R- 2.47	R- 0.14
R-30.64	R- 1.03	R- 0.64	R- 2.47	R- 0.14
3M-30.71	3M- 1.16	3M- 0.64	3M- 2.43	3M- 0.18
3M-31.32	3M- 1.18	3M- 0.67	3M- 2.55	3M- 0.21
X=30.68	X= 1.10	X= 0.65	X= 2.48	X= 0.17
RSD=1.7%	RSD= 7.3%	RSD= 3.1%	RSD= 2.0%	RSD=17.6%

Discussion of Results

As can be seen from examining the results, there is excellent correlation between the two methods. The OVM's generally measure about 6% higher than the charcoal tubes. In addition, since the Y-intercept is less than 0.1, even at very low concentrations, the ratio of OVM result to charcoal tube result remains consistent. The important point to consider is that neither method is necessarily correct, but that they are highly correlatable.

The regression equations and correlation coefficients for the indoor and outdoor samples show there is essentially no difference between the two. Although the effort has not been made to prove this statistically, it appears to be the case. This demonstrates that in most indoor situations there is sufficient air movement to assure that diffusion within the OVM is the rate-limiting mode of transport.

The samples that were collected in November have been temperature corrected. Although in general the OVM is fairly temperature independent (it varies directly with the square root of the ratio to standard temperature), the difference between the OVM's and charcoal tubes is temperature dependent to a greater degree. This is due to the charcoal tube results varying inversely with the ratio to standard temperature. The overall result is the difference varies with the three halves power of the temperature ratio [Difference $(T/T_s)^{3/2}$]. The temperatures on the sample days in November ranged from 15°to 25°C below standard temperature. At 0°C the charcoal tube results are approximately 14% high relative to the OVM results if left uncorrected.

As seen in Table II the precision of our OVM's is very good. Typical charcoal tube relative standard deviations are approximately 10-15%. Most of the variation is due to varying pump performance, and the elimination of the pump from the sample collection process aids precision.

In addition to benzene, toluene and xylene, other organic vapors (mostly heavier compounds) exist in the by-products area. The data show that the existence of mixed vapor systems does not significantly affect the performance of a diffusion device versus that of an active sampling device in the determination of benzene concentrations.

The major advantage to the use of the OVM in the field is the absence of a sampling pump. Thus, pump mechanical problems no longer are a concern. In addition, pump calibration and maintenance time is minimized. Also, the OVM offers less physical hindrance to a worker than a pump and sampling train. 3M is currently making some packaging changes which should make the units easier to use in the field.

Conclusions

(1) An almost perfect correlation exists between the charcoal tube method and the OVM method for the determination of benzene concentrations in air.

(2) The OVM method gives results approximately 6% higher than the tube method.

(3) There is sufficient air movement indoors to allow the OVM to function correctly.

Conclusions (Cont'd.)

(4) Mixed vapor systems do not affect the OVM differently than charcoal tubes.

(5) The OVM is at least as precise as the charcoal tube method.

(6) The OVM is more reliable in the field than the charcoal tube/pump combination.

Recommendations

(1) The 3M Organic Vapor Monitor should be used for the determination of personal and area exposures to benzene.

(2) Additional data for toluene and xylene should be analyzed in manner similar to that for benzene.

TABLE III

Individual Sample Results - Benzene

Sample No	Test Date	Indoor or Outdoor Building	Charcoal Tube (ppm)	3M OVM (ppm)
1	7 June	Out	0.21	0.20
2	"	Out	0.07	0.07
3	"	Out	0.13	0.14
4	"	In	1.11	1.10
5	"	In	2.77	2.47
6	"	In	0.39	0.35
7	"	In	0.62	0.64
8	"	Out	0.47	0.53
9	"	Out	0.75	0.83
10	8 June	In	0.21	0.42
11	"	"	0.81	1.21
12	"	"	0.28	0.41
13	"	"	2.64	2.85
14	"	"	0.91	0.95
15	"	"	0.30	0.49
16	9 June	Out	1.81	1.93
17	"	"	0.84	0.91
18	"	"	7.98	8.82
19	"	"	2.09	2.23
20	"	"	21.55	23.55
21	"	"	22.04	22.43
22	"	"	75.42	81.93
23	"	"	29.13	33.09
24	14 June	In	0.60	0.56
25	"	"	0.42	0.50
26	"	"	0.55	0.56
27	20 June	Out	10.02	9.60
28	"	"	30.17	30.34
29	"	"	90.73	94.05
30	"	"	13.22	15.79
*31	21 June	In	2.12	2.57
*32	"	"	1.73	1.94
33	17 August	In	0.14	0.22
34	"	"	0.45	0.59
35	"	"	1.46	2.17
36	"	"	1.23	1.26
37	"	Out	5.81	6.78
38	"	"	0.18	0.23
39	"	"	0.03	0.00
40	"	"	3.64	4.61
41	"	"	1.57	2.04

TABLE III

Individual Sample Results - Benzene

Sample No.	Test Date	Indoor or Outdoor Building	Charcoal Tube (ppm)	3M OVM (ppm)
42	8 November	In	0.00	0.00
43	"	"	0.15	0.00
44	"	"	0.56	0.52
45	"	"	0.07	0.00
46	"	"	47.30	49.71
47	"	"	35.32	42.06
48	"	Out	0.66	0.61
49	"	"	2.27	2.72
50	"	"	9.61	11.08
51	9 November	In	0.48	0.50
52	"	"	0.55	0.57
53	"	"	1.07	1.22
54	"	Out	2.88	3.58
56	"	"	4.38	5.28
56	"	"	1.41	1.59
57	"	"	1.63	1.71
58	"	"	5.22	6.00
59	"	"	4.59	4.84
60	"	In	1.50	1.45
61	20 November	Out	6.78	7.49
62	"	"	7.62	8.76
63	"	"	2.81	2.79
64	"	"	2.91	2.81
65	"	"	1.99	1.91
66	"	"	1.87	1.07
67	"	"	2.88	1.86
68	"	"	3.68	3.75
69	"	"	22.10	22.20
70	21 November	In	8.75	8.80
71	"	"	15.80	17.80
72	"	"	40.60	42.20
73	"	Out	0.78	0.89
74	"	"	38.30	41.30
75	"	"	1.58	2.00
76	"	"	7.20	7.63
77	"	"	0.48	0.40
78	"	"	0.87	0.90
79	"	"	0.44	0.74

*Personal Samples
Note: Samples #42 - 70 have been temperature corrected.

3M Occupational Health and Environmental Safety Division

3M Center
St. Paul, Minnesota 55144-1000
612/733 1110

October 16, 1992

3M

Mark Puskar
Abbott Laboratories, D-38A
1401 Sheridan Rd
North Chicago, IL 60064

Dear Mark:

I want to apologize for the delay in responding to your methylene chloride study. We would like to participate in the study, however it should be noted that our 3M 3520 Organic Vapor Monitor has limitations.

The monitor has a maximum capacity of 3000 micrograms at high relative humidities (i.e., >60%). This capacity will increase as relative humidity drops. Based on a capacity of 3000 micrograms, the maximum concentration measurements are as follows:

15 minutes:	1518 ppm
240 minutes:	120 ppm
480 minutes:	60 ppm

Based on this information we recommend that sampling be limited to four hours when methylene chloride concentrations are unknown. However, if concentrations are expected to be at the TLV (50 ppm) or below, the use of the 3520 monitor is acceptable.

The validation study that Abbott outlined calls for a sampling site that is greater then 50 ppm methylene chloride. If an 8 hour sample was collected at this location, it is feasible that the capacity of the monitor may be exceeded. This sampling site pushes the limitation of the monitor. However, all of the other sampling sites, including the sampling times, fall within the limitations of the 3M 3520 monitor. We would like to participate in the study, however, we want to caution you that our 3M 3520 monitor cannot be used in all situations, just like most other sampling devices.

Per our discussion, we have spiked organic vapor monitors with methylene chloride. We have four sets with triplicates in each set. The methylene chloride concentrations are as follows:

Set A:	1330 microgram
Set B:	265 microgram
Set C:	530 microgram
Set D:	2650 micrograms
Set F:	Blanks

If you have any questions, please feel free to give me a call at 612-737-4459. I look forward to working with you and Abbott in the future.

Regards,

Robert A. Weber, CIH
Technical Service Representative
3M Occupational Health & Environmental Safety Division

RAW:llj/54
Enclosure

3M
Organic Vapor Monitor

Summary of Technical Data

Correlation With Charcoal Tubes

Methylene Chloride
Acetone
Methyl Acetate
Pentane

Comparison of Diffusional Organic Vapor Monitors with Charcoal Tubes for Sampling Laboratory Challenges to Contaminant Mixtures

Laboratory Performance of Passive Personal Samplers for Waste Anesthetic Gas (Enflurane)oncentrations

Field comparison of Charcoal Tubes and Passive Vapor Monitors with Mixed Organic Vapors

Sampling Variable Concentration

Toluene
Mixture (MEK/Hexane/Ethyl Benzene/1,1,2,2 Tetrachloroethane)
Mixture (Toluene/MEK/TCE/Hexane/Ethyl Acetate)

Sampling High Vapor Pressure Compounds

Vinyl Chloride
Pentane
Dichloromethane
Acetone
Methyl Acetate

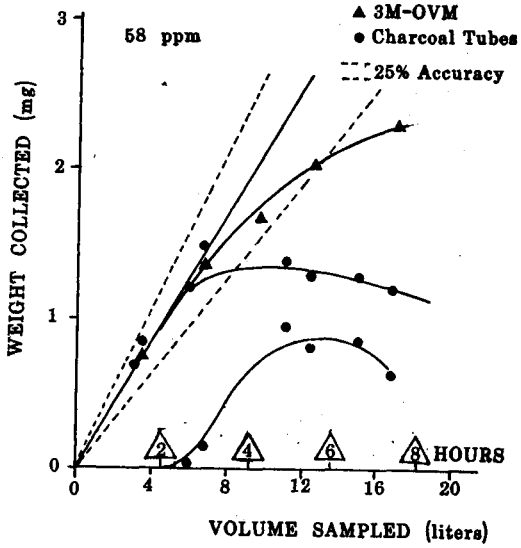
CORRELATION

WITH CHARCOAL TUBES

3M 110845

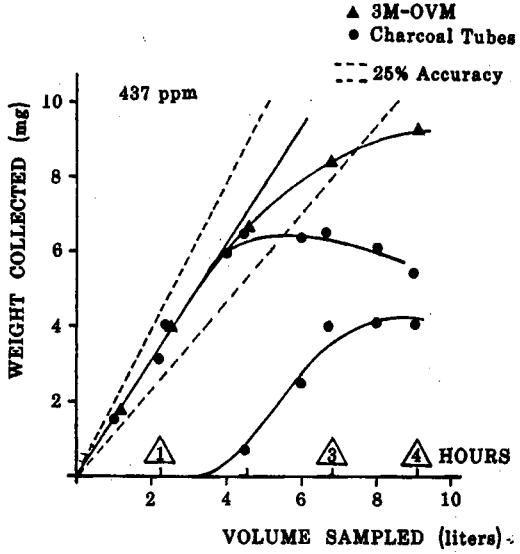
METHYLENE CHLORIDE

RH-85%

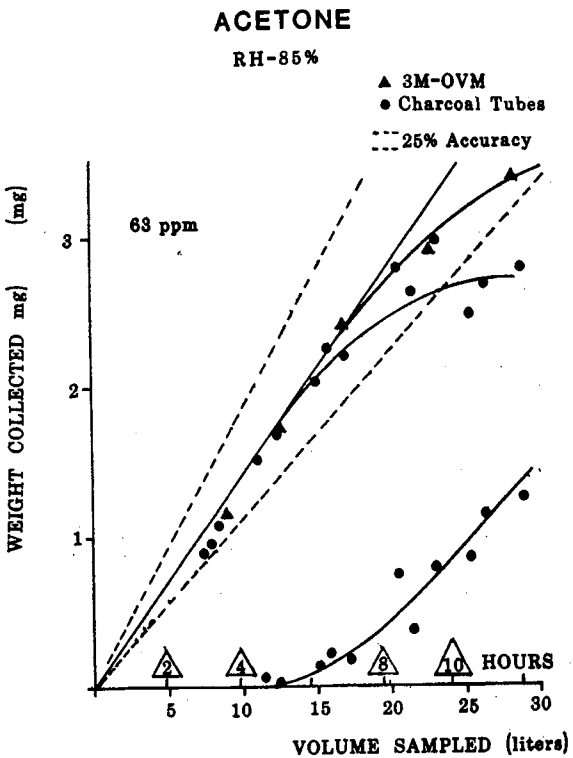


METHYLENE CHLORIDE

RH-85%

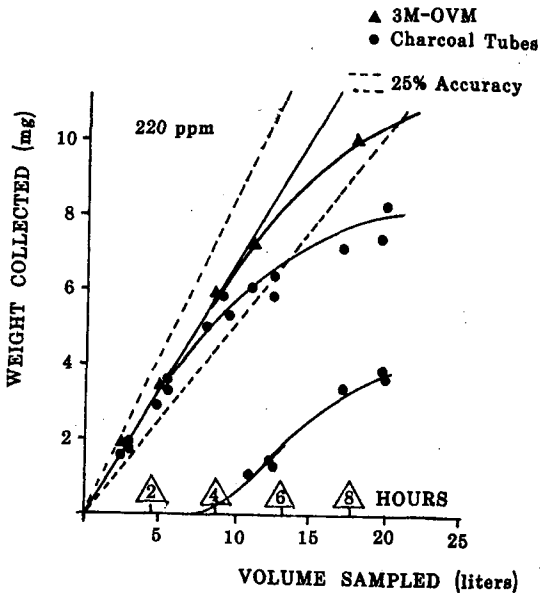


3M 110847


ACETONE
RH-85%
▲ 3M-OVM
● Charcoal Tubes
25% Accuracy
63 ppm
WEIGHT COLLECTED mg) (mg)
1
2
3
2
4
8
10
HOURS
5
10
15
20
25
30
VOLUME SAMPLED (liters)

3M 110848

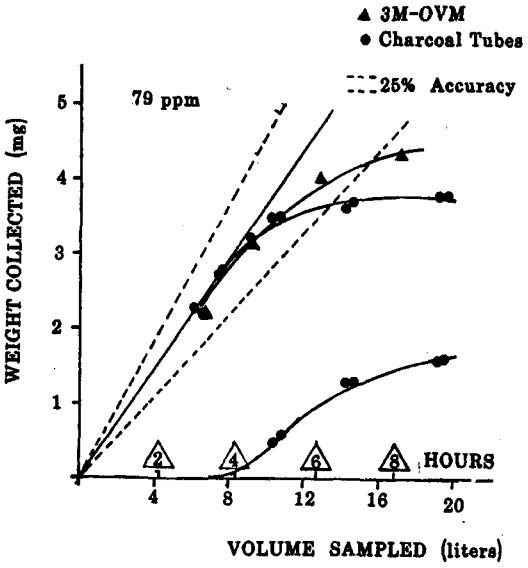
METHYL ACETATE



3M 110849

PENTANE

RH-85%



COMPARISON OF DIFFUSIONAL ORGANIC VAPOR MONITORS WITH CHARCOAL TUBES FOR SAMPLING LABORATORY CHALLENGES TO CONTAMINANT MIXTURES.

Anders, L. W. and Mullins, H.E., Occupational Health & Safety Products Division, 3M Company, St. Paul, Minnesota 55144.

ABSTRACT

Because most industrial environments contain numerous contaminants, a laboratory evaluation compared performance of diffusional organic vapor monitors to charcoal tubes when sampling mixtures of known concentrations. The challenges consisted of a binary mixture of toluene and methyl ethyl ketone and a tertiary mixture of benzene, toluene and xylene. Unleaded gasoline and unleaded gasoline containing various alcohols, e.g. ethanol, methanol and t-butyl alcohol were the complex mixtures used in the evaluation. The results of each sampling technique are correlated with the challenges of known concentrations.

COMPARISON OF DIFFUSIONAL ORGANIC VAPOR MONITORS WITH CHARCOAL TUBES FOR SAMPLING LABORATORY CHALLENGES TO CONTAMINANT MIXTURES.

ANDERS, L.W. AND MULLINS, H.E. OCCUPATIONAL HEALTH & SAFETY PRODUCTS DIVISION, 3M COMPANY SAINT PAUL, MINNESOTA 55144.

INTRODUCTION

Diffusional sampling devices such as the 3M Organic Vapor Monitor (OVM) offer many advantages for measuring concentration levels of industrial contaminants because they are lightweight, require no power, pump or tubing and are not likely to impede the work activity of the user.

Because these sampling devices could replace the conventional pump and charcoal tubes for sampling the industrial environment, this evaluation compared the precision and accuracy of the charcoal tubes to the 3M-Organic Vapor Monitors. A selected set of simple and complex mixtures were used to generate air concentrations normally found in the industrial environment. This evaluation consisted entirely of sampling laboratory generated air concentrations of the contaminant mixtures. Evaluating the precision and accuracy of these two sampling techniques is in keeping with the NIOSH Standards Completion Program where the precision and accuracy of the charcoal tubes were validated by sampling known air concentrations of organic vapor contaminant from a laboratory generation system.

PROCEDURE

To evaluate and compare the sampling performance of charcoal tubes to the 3M Organic Vapor Monitors, known air concentrations were generated for simple and complex mixture in a laboratory generator-dilution system. This system as illustrated in Figure 1, consists of a calibrated dry air gas meter, a syringe device mechanism to deliver th liquid contaminant mixture to a heated manifold, and a device to hold eighteen (18) charcoal tubes or monitors. The air concentration can be determined by measuring the initial and final weight of the syringe containing the liquid contaminant and measuring the total air volume during a sampling period of known time.

The evaluation consisted of two parts; Part I - Comparison of Charcoal Tubes to 3M - Organic Vapor Monitor (OVM) when Sampling Contaminant Mixtures at Constant Concentrations, and Part II - Comparison of Charcoal Tubes to 3M - Organic Vapor Monitor (OVM) when Sampling Contaminant Mixtures at Variable Concentrations. In Part I, mixtures and desired concentrations used for the comparison are tabulated in Table I. In this part of the evaluation, three (3) charcoal tubes and three (3) 3M - Organic Vapor Monitors samples were collected at intervals of one (1), two (2), three (3), five (5), six (6) and seven (7) hours. For each mixture, the thirty six (36) samples (18 - charcoal tubes and 18 - 3M Organic Vapor monitors) were collected during an eight hour sampling period. The time-weighted-average

concentration during the eight hour period was determined by measuring the total air volume and the weight of the liquid contaminant mixture delivered to the heated air manifold measuring the syringe/liquid contaminant weight at the beginning and at the end of the sampling period. Eighteen (18) samples could be collected simultaneously, therefore, the following sampling profile allowed the thirty six (36) samples to be collected in an eight hour period. The one hour samples were followed by the seven hour samples, the two hour samples followed by the six hour samples, and the three hour samples followed by the five hour samples. In order to compare the results with the known time-weighted-average concentration for the eight hour period as determined by mass balance of the air flow and liquid contaminant flow to the heated manifold, the results of the following data sets must be combined. The results of one hour samples combined with the seven hour samples, the two hour samples combined with the six hour samples and the three hour samples combined with the five hour samples. Although the results of the above sample sets had to be combined to compare them to the time-weighted-average concentration determined by mass balance of the laboratory generation system, a comparison of the charcoal tube results can be compared to the 3M - Organic Vapor Monitor results for each of sampling intervals.

In Part II, the mixtures and desired concentrations sampled for the evaluation are tabulated in Table II. The evaluations in Part II are divided into exposure profile A where a contaminant mixture is sampled for one hour followed by sampling air with a zero concentration of the

contaminant mixture for one hour. This sequence was repeated four times. In exposure profile B, a contaminant mixture is sampled for one hour, then air with a zero concentration of the contaminant mixture is sampled for three hours. This sequence was repeated. In both profiles, the total sampling period was eight hours with the difference being in profile A, where the contaminant mixture concentration is sampled for four hours while in profile B, the contaminant mixture concentration is sampled for only two hours.

In this part of the evaluation, the variable concentrations were sampled to evaluate if any sample loss occurs during the sampling period when the contaminant mixture concentration was zero.

ANALYTICAL PROCEDURES

After sample collection, the 3M-Organic Vapor Monitor and the charcoal tubes were capped and stored at ambient temperatures. The recovery coefficients were determined for the 3M-Organic Vapor Monitor according to the recommended procedure. The recovery coefficient for the charcoal tubes were also determined by spiking the liquid mixture on a filter paper and allowing the charcoal to collect the organic vapors. After desorbing the samples with carbon disulfide, the analysis was performed using a Hewlett Packard (5840A) gas chromatograph equipped with a flame ionization detector. For the gasoline samples, the total integrated area was used to determine the sample weight.

For the charcoal tubes, the sampling rates were determined by calibration of critical orifices which ranged from 30-45 cubic centimeters per minute. For the 3M-Organic Vapor Monitor, the sampling rates for gasoline and naphtha were determined in separate experiments by measuring the weight collection rate from a challenge of known concentration. The sampling rates and recovery coefficients are tabulated in Table III.

Results and Discussion

PART I - COMPARISON OF CHARCOAL TUBES TO 3M - ORGANIC VAPOR MONITOR (OVM) WHEN SAMPLING CONTAMINANT MIXTURES AT CONSTANT CONCENTRATIONS.

The results of sampling a toluene/methyl ethyl ketone mixture are summarized and tabulated in Table IV. For toluene, there is excellent correlation of the results of charcoal tube samples and the 3M - Organic Vapor Monitor samples for each of the sampling intervals. The time-weighted-average concentrations as determined by the combined results of each sample set (18 samples) was 186 mg/m^3 measured by the 3M - Organic Vapor Monitor and 176 mg/m^3 measured by the charcoal tubes. When compared to the concentration as determined by the mass balance of the generation system, these results are 97% and 92% of the concentration for 3M-Organic Vapor Monitor and charcoal tubes respectively.

For methyl ethyl ketone, the results of the charcoal tubes are very low and compare poorly with those of the 3M - Organic Vapor monitor. For the 3M - Organic Vapor Monitor, the time-weighted-average concentration

determined by the combined sample set (18) was 144 mg/m^3. This is 104% of the concentration determined by mass balance of the generation system. For the charcoal tubes, the time-weighted-average concentration determined by the combined sample set (18) was 50 mg/m^3 or 36% of the concentration determined by mass balance of the generation system. These charcoal tubes were not overloaded, in fact, no methyl ethyl ketone was found in the back section of the charcoal tubes.

In Table V, the results of sampling a benzene/toluene/xylene mixture are summarized and tabulated. For each of the contaminants in the mixture, there is excellent correlation of the charcoal tube with the 3M - Organic Vapor Monitor at all sampling intervals. The total time-weighted-average concentration determined by combining the eighteen (18) samples collected by each technique enables an assessment of the accuracy by comparison with the concentration determined by mass balance of generation system. For benzene, the results are 91% and 97% for the 3M - Organic Vapor Monitor and charcoal tubes respectively when comparing to the mass balance concentration. For toluene, the results are 90% and 95% and for xylene the results are 87% and 91% for the 3M - Organic Vapor Monitor and charcoal tubes respectively for each data set.

In Table VI, the results of sampling a complex mixture, VM & P Naphtha, are summarized and tabulated. There is excellent correlation of the charcoal tubes with the 3M - Organic Vapor Monitor at each of the sampling intervals. The accuracy is also excellent as determined by

comparing the time-weighted-average concentration with the concentration determined by the mass balance of the generation system. When combining all eighteen (18) samples collected by one technique, the accuracy is 95% and 97% for the 3M - Organic Vapor Monitor and charcoal tubes respectively.

Unleaded gasoline was sampled at two concentrations, 42 mg/m^3 and 96 mg/m^3. These results are summarized and tabulated in Tables VII and VIII. Again, the correlation of the two sampling techniques is excellent. The accuracy as determined by comparing the time-weighted-average of the eighteen (18) samples collected by each technique and the concentration as determined by the mass balance of the generation system was at, the low concentration (42 mg/m^3), 91% and 95% and, at the high concentration (96 mg/m^3), 97% and 101% for the 3M - Organic Vapor Monitor and the charcoal tubes respectively in each of the evaluations.

Unleaded gasoline blended with ethanol and unleaded gasoline blended with methanol and tert-butyl alcohol were also sampled as complex mixtures. The results are summarized and tabulated in Tables IX and X. Again, the correlation of the two sampling techniques is excellent. In gasoline/ethanol, the accuracy was 101% and 103% for the 3M - Organic Vapor monitor and the charcoal tubes. For the gasoline/methanol/TBA, the accuracy was 96% and 103% for the 3M - Organic Vapor Monitor and the charcoal tubes. The accuracy of each sampling technique is again compared to the concentration determined by the mass balance of the generation system.

Part II - COMPARISON OF CHARCOAL TUBES TO 3M - ORGANIC VAPOR MONITOR (OVM) WHEN SAMPLING CONTAMINANT MIXTURES AT VARIABLE CONCENTRATIONS.

For this part of the evaulation, the variable concentrations were generated in two ways. The results are summarized and tabulated in Table XI for samples collected when sampling a high concentration of the contaminant mixture on one hour followed by sampling a zero concentration for three hours. This sequence was repeated so that the samples collected the high concentration for a two hour period. For the six simple and complex mixtures listed in Table II, it can be observed that the sample collected with the charcoal tubes have xcellent correlation with those collected with the 3M - Organic Vapor Monitor with the exception of methyl ethyl ketone in the toluene/methyl k tone mixture. It can be noted that the charcoal tubes greatly underestimates the methyl ethyl ketone concentration. Besides the excellent correlation between the two sampling techniques, both techniques also have acceptable accuracy when comparing the concentration measured by the 3M - Organic Vapor Monitor and the charcoal tubes to the concentration determined from the mass balance of the generation system.

In Table XII, the results are summarized and tabulated for samples collected when sampling a high concentration for one hour followed by sampling zero concentration for one hour and a repeat of this sequence four times. With the exception of the charcoal tube estimation of the methyl ethyl ketone concentration in the toluene/methyl ethyl ketone mixture, all the resultstabulated in Table XII indciate again the

excellent correlation of the charcoal tubes results with the 3M - Organic Vapor monitor results of measuring the concentration of the six simple and complex mixtures. Both techniques also have acceptable accuracy as determined by comparing the concentrations measured by the 3M - Organic Vapor Monitor and the charcoal tubes with the concentration determined by the mass balance of the generation system.

Conclusions

From these laboratory evaluations, the 3M - Organic Vapor Monitor was able to sample and determine the concentration of a representative set of simple and complex mixtures with excellent precision and accuracy. The charcoal tubes also measured the same mixtures with excellent precision and accuracy with the exception of methyl ethyl ketone in the toluene/methyl ethyl ketone mixture.

TABLE I - Simple and Complex Mixtures Generated for Part I of the Evaluation.

	Mixture	Concentrations (mg/m^3)	(ppm)
I-1	Toluene/Methyl Ethyl Ketone	147/147	50/50
I-2	Benzene/Toluene/Xylene	3/15/22	1/5/5
I-3	Naphtha (VM & P)	204	50
I-4	Gasoline (unleaded)	49	10
I-5	Gasoline (unleaded)	123	25
I-6	Gasoline/Ethanol	123	25
I-7	Gasoline/Methanol/TBA	123	25

TABLE II - Simple and Complex Mixtures Generated for Part II of the Evaluation.

	Mixture	Concentration (mg/m^3)	(ppm)
II-1	Toluene/Methyl Ethyl Ketone	147/147	50/50
II-2	Benzene/Toluene/Xylene	30/150/220	10/50/50
II-3	Naphtha (VM & P)	204	50
II-4	Gasoline (unleaded)	1230	250
II-5	Gasoline (Ethanol)	1230	250
II-6	Gasoline/Methanol/TBA	1230	250

TABLE III - Sample Rates and Recovery Coeficients

Compound	Sampling Rate 3M-OVM	Recovery Coefficient 3M-OVM	Recovery Coefficient Charcoal Tube
Benzene	35.5 ± .6	1.02	1.02
Xylene	27.3 ± .5	1.07	.99
Toluene	31.4 ± .6	1.05	1.01
Methyl Ethyl Ketone	36.3 ± .9	1.00	.86
Naphtha	33.2 ± .7	1.04	.99
Gasoline	31.0 ± .6	1.05	.99

E IV - Toluene/Methyl Ethyl Ketone

Length of Sampling Period (min.)	Sample Type and Number of Samples	Measured Concentration (mg/m^3) Toluene	Methyl Ethyl Ketone
60	3M-OVM (3)	198 ± 6	137 ± 5
(0-60)	CT (3)	182 ± 6	34 ± 11
500	3M-OVM (3)	186 ± 4	153 ± 6
(60-560)	CT (3)	176 ± 5	61 ± 4
Time-Weighted - Average Concentration	3M-OVM (6)	187 (98%)	151 (109%)
	CT (6)	177 (92%)	58 (42%)
120	3M-OVM (3)	202 ± 6	140 ± 6
(0-120)	CT (3)	162 ± 14	30 ± 3
440	3M-OVM (3)	182 ± 2	140 ± 4
(120-560)	CT (3)	182 ± 5	53 ± 4
Time-Weighted- Average Concentration	3M-OVM (6)	186 (97%)	140 (101%)
	CT (6)	178 (93%)	48 (35%)
180	3M-OVM (3)	189 ± 2	132 ± 4
(0-180)	CT (3)	168 ± 13	37 ± 3
380	3M-OVM (3)	183 ± 2	147 ± 9
(180-560)	CT (3)	176 ± 4	49 ± 6
Time-Weighted- Average Concentration	3M-OVM (6)	184 (96%)	142 (102%)
	CT (6)	173 (90%)	45 (32%)
Total Time-W ighted- Average Concentration	3M-OVM (18)	186 (97%)	144 (104%)
	CT (18)	176 (92%)	50 (36%)
Concentration from Mass Balance of Generation System		192 (51/ppm)	139 (47 ppm)

LE V - Benzene/Toluene/Xylene

Length of Sampling Period (min.)	Sample Type and Number of Samples	Measured Concentration (mg/m^3) Benzene	Toluene	Xylene
60	3M-OVM (3)	12 ± 1	53 ± 1	53 ± 1
(0-60)	CT (3)	12 ± 1	63 ± 11	62 ± 10
435	3M-OVM (3)	5.0 ± .2	23 ± 1	25 ± 1
0-495)	3M-OVM (3)	5.4 ± 1	25 ± 2	26 ± 2
e-Weighted -	SM-OVM (6)	5.9 (96%)	27 (93%)	28 (93%)
verage Concentration	CT (6)	6.2 (102%)	30 (103%)	30 (100%)
125	3M-OVM (3)	7.3 ± .2	37 ± 1	34 ± 1
)	CT (3)	9.1 ± 2	42 ± 8	42 ± 8
370	3M-OVM (3)	4.6 ± .3	22 ± 2	22 ± 2
5-495)	CT (6)	4.7 ± 1	21 ± 2	21 ± 2
ime-W ighted-	3M-OVM (6)	5.3 (87%)	26 (90%)	25 (83%)
verage Concentration	CT (6)	5.8 (95%)	25 (90%)	26 (87%)
180	3M-OVM (3)	6.7 ± .1	31 ± 1	31 ± 1
-180)	CT (3)	7.2 ± 1	33 ± 5	32 ± 5
315	3M-OVM (3)	4.6 ± .2	22 ± 1	22 ± 1
0-495)	CT (3)	4.9 ± 1	23 ± 2	23 ± 2
me-Weighted-	3M-OVM (6)	5.4 (89%)	25 (86%)	25 (83%)
erage Concentration	CT (6)	5.7 (93%)	27 (93%)	26 (91%)
al				
me-Weighted-	3M-OVM (18)	5.5 (91%)	26 (90%)	26 (87%)
erage Concentration	CT (18)	5.9 (97%)	28 (95%)	27 (91%)
ncentration from ss Balance of ion System		6.1 (1.9ppm)	29 (7.7 ppm)	30 (6.9 ppm)

BLE VI - Naphtha (VM & P) 236 mg/m^3 (58 ppm)

Length of Sampling Period (min.)	Sample Type and Number of Samples	Measured Concentration (mg/m^3) Naphtha (VM & P)
60	3M-OVM (3)	219 ± 2
(0-60)	CT (3)	191 ± 33
420	3M-OVM (3)	247 ± 4
60-480)	CT (3)	251 ± 5
me-Weighted - Average Concentration	3M-OVM (6)	243 (103%)
	CT (6)	243 (103%)
120	3M-OVM (3)	284 ± 10
0-120)	CT (3)	289 ± 20
60	3M-OVM (3)	181 ± 5
120-480)	CT (3)	190 ± 5
Time-Weighted- Average Concentration	3M-OVM (6)	207 (88%)
	CT (6)	214 (91%)
180	3M-OVM (3)	291 ± 3
0-180)	CT (3)	289 ± 12
300	3M-OVM (3)	189 ± 7
180-480)	CT (3)	190 ± 10
Time-Weighted- Average Concentration	3M-OVM (6)	225 (95%)
	CT (6)	244 (103%)
otal Time-Weighted- Average Concentration	3M-OVM (18)	225 (95%)
	CT (18)	228 (97%)
Concentration from Mass Balance of ation System		236 (58 ppm)

BLE VII - Gasoline (Unleaded) (42 mg/m^3)

Length of Sampling Period (min.)	Sample Type and Number of Samples	Measured Concentration (mg/m^3) Gasoline (Unleaded)
60	3M-OVM (3)	52 ± 2
(0-60)	CT (3)	54 ± 9
375	3M-OVM (3)	37 ± 2
(60-435)	CT (3)	39 ± 1
Time-Weighted - Average Concentration	3M-OVM (6)	39 (93%)
	CT (6)	41 (98%)
120	3M-OVM (3)	44 ± 1
(0-120)	CT (3)	47 ± 10
315	3M-OVM (3)	37 ± 1
120-435)	CT (3)	36 ± 2
Time-Weighted- Average Concentration	3M-OVM (6)	38 (91%)
	CT (6)	30 (93%)
180	3M-OVM (3)	42 ± 1
(0-180)	CT (3)	44 ± 1
255	3M-OVM (3)	36 ± 1
180-435)	CT (3)	38 ± 1
Time-Weighted- Average Concentration	3M-OVM (6)	38 (91%
	CT (6)	40 (95%)
Total Time-Weighted- Average Concentration	3M-OVM (18)	38 (91%)
	CT (18)	40 (95%)
Concentration from Mass Balance of Generation System		42 (8.5 ppm)

TABLE VIII - Gasoline (Unleaded) (96 m/m^3)

Length of Sampling Period (min.)	Sample Type and Number of Samples	Measured Concentration (mg/m^3) Gasoline (Unleaded)
60 (0-60)	3M-OVM (3)	93 ± 7
	CT (3)	87 ± 3
420 (60-480)	3M-OVM (3)	92 ± 3
	CT (3)	95 ± 5
Time-Weighted Average Concentration	3M-OVM (6)	92 (96%)
	CT (6)	94 (98%)
120 (0-120)	3M-OVM (3)	93 ± 3
	CT (3)	95 ± 7
360 (120-480)	3M-OVM (3)	91 ± 4
	CT (3)	96 ± 4
Time-Weighted Average Concentration	3M-OVM (6)	91 (95%)
	CT (6)	96 (100%)
175 (0-175)	3M-OVM (3)	93 ± 1
	CT (3)	99 ± 3
305 (175-480)	3M-OVM (3)	96 ± 5
	CT (3)	103 ± 3
Time-Weighted Average Concentration	3M-OVM (6)	92 (96%
	CT (6)	102 (106%)
Total Time-Weighted Average Concentration	3M-OVM (18)	93 (97%)
	CT (18)	97 (101%)
Concentration from Mass Balance of Generation System		96 (19.5 ppm)

ABLE IX - Gasoline (Ethanol) (125 mg/m^3)

Length of Sampling Period (min.)	Sample Type and Number of Samples	Measured Concentration (mg/m^3) Gasoline (Ethanol)
60 (0-60)	3M-OVM (3)	106 ± 5
	CT (3)	114 ± 15
420 (60-480)	3M-OVM (3)	130 ± 4
	CT (3)	133 ± 8
Time-Weighted - Average Concentration	3M-OVM (6)	127 (102%)
	CT (6)	131 (105%)
120 (0-120)	3M-OVM (3)	113 ± 3
	CT (3)	114 ± 5
360 (120-480)	3M-OVM (3)	129 ± 7
	CT (3)	129 ± 16
Time-Weighted- Average Concentration	3M-OVM (6)	125 (100%)
	CT (6)	125 (100%)
180 (0-180)	3M-OVM (3)	113 ± 5
	CT (3)	116 ± 2
300 (180-480)	3M-OVM (3)	134 ± 3
	CT (3)	139 ± 5
Time-Weighted- Average Concentration	3M-OVM (6)	126 (101%)
	CT (6)	130 (104%)
Total Time-Weighted- Average Concentration	3M-OVM (18)	126 (101%)
	CT (18)	129 (103%)
Concentration from Mass Balance of Generation System		125 (25.4 ppm)

ABLE X - Gasoline (Methanol/TBA)

Length of Sampling Period (min.)	Sample Type and Number of Samples	Measured Concentration (mg/m^3) Gasoline (Methanol/TBA)
60 (0-60)	3M-OVM (3)	94 ± 1
	CT (3)	86 ± 10
420 (60-480)	3M-OVM (3)	112 ± 2
	CT (3)	124 ± 4
Time-Weighted - Average Concentration	3M-OVM (6)	110 (97%)
	CT (6)	119 (105%)
120 (0-120)	3M-OVM (3)	102 ± 3
	CT (3)	101 ± 2
360 (120-480)	3M-OVM (3)	108 ± 5
	CT (3)	119 ± 1
Time-Weighted- Average Concentration	3M-OVM (6)	107 (95%)
	CT (6)	115 (102%)
180 (0-180)	3M-OVM (3)	102 ± 4
	CT (3)	103 ± 6
300 (120-480)	3M-OVM (3)	116 ± 2
	CT (3)	122 ± 4
Time-Weighted- Average Concentration	3M-OVM (6)	111 (98%)
	CT (6)	115 (102%)
Total Time-Weighted- Average Concentration	3M-OVM (18)	109 (96%)
	CT (18)	116 (103%)
Concentration from Mass Balance of Generation System		113 (22.9 ppm)

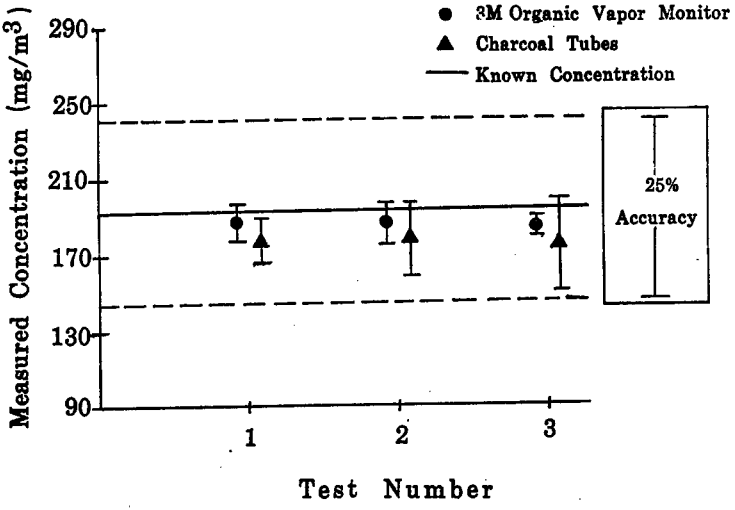
le XI - Variable Challenge Concentrations According to Profile A

ture pled	Length of Sampling Period (min.)	Concentration from Mass Balance of Generation System (mg/m^3)	Sample Type and Number of Samples	Measured Concentration (mg/m^3)
1 Toluene/ thyl Ethyl tone	120	228	Toluene	
			3M-OVM (4)	231 ± 3 (101%)
			CT (4)	217 ± 10 (95%)
		178	Methyl Ethyl Ketone	
			3M-OVM (4)	144 ± 11 (81%)
			CT (4)	48 ± 1 (27%)
2 Benzene/ luene/ lene	120	47	Benzene	
			3M-OVM (4)	45 ± 1 (96%)
			CT (4)	44 ± 1 (94%)
		222	Toluene	
			3M-OVM (4)	207 ± 6 (93%)
			CT (4)	217 ± 4 (98%)
		227	Xylene	
			3M-OVM (4)	222 ± 7 (98%)
			CT (4)	224 ± 4 (99%)
3 Naphtha	155	212	3M-OVM (9)	214 ± 5 (101%)
			CT (9)	228 ± 11 (108%)
4 Gasoline (unleaded)	120	1,000	3M-OVM (4)	957 ± 38 (96%)
			CT (9)	979 ± 14 (98%)
5 Gasoline/ Ethanol	120	1,011	3M-OVM (4)	1065 ± 61 (105%)
			CT (4)	1197 ± 38 (118%)
6 Gasoline/ Methanol/ TBA	120	1,011	3M-OVM (4)	981 ± 48 (97%)
			CT (4)	982 ± 53 (97%)

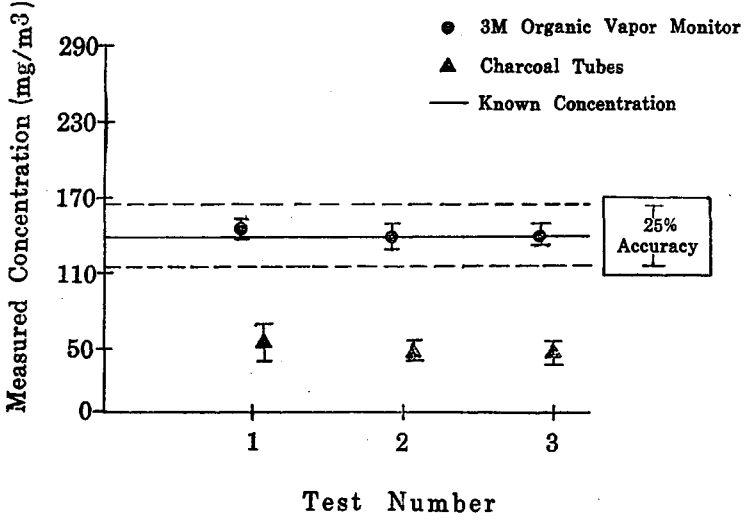
ble XII - Variable Challenge Concentrations According to Profile B

ture pled	Length of Sampling Period (min.)	Concentration from Mass Balance of Generation System (mg/m^3)	Sample Type and Number of Samples	Measured Concentration (mg/m^3)
-1 Toluene/ thyl Ethyl tone	240	206	Toluene	
			3M-OVM (4)	226 ± 3 (110%)
			CT (4)	226 ± 6 (110%)
		161	Methyl Ethyl Ketone	
			3M-OVM (4)	155 ± 10 (96%)
			CT (4)	67 ± 3 (42%)
-2 Benzene/ oluene/ ylene	240	47	Benzene	
			3M-OVM (4)	46 ± 3 (97%)
			CT (4)	43 ± 2 (92%)
		223	Toluene	
			3M-OVM (4)	211 ± 15 (95%)
			CT (4)	203 ± 8 (95%)
		228	Xylene	
			3M-OVM (4)	227 ± 30(100%)
			CT (4)	209 ± 9 (92%)
-3 Naphtha	240	176	3M-OVM (4)	176 ± 4 (100%)
			CT (4)	183 ± 13(103%)
-4 Gasoline (unleaded)	240	906	3M-OVM (4)	807 ± 32 (89%)
			CT (4)	890 ± 30 (98%)
-5 Gasoline/ Ethanol	240	897	3M-OVM (4)	933 ± 32(104%)
			CT (4)	1003 ± 70 (112%)
-6 Gasoline/ Methanol/ TBA	240	888	3M-OVM (4)	830 ± 41 (93%)
			CT (4)	772 ± 73 (87%)

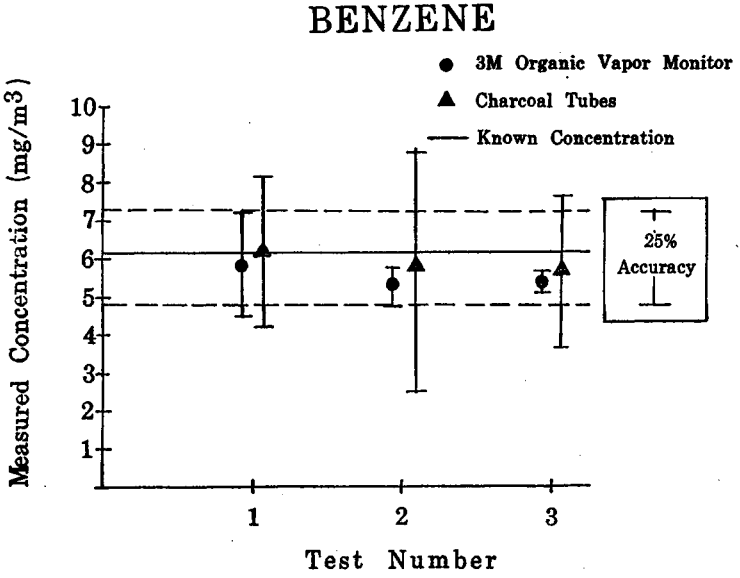
TOLUENE



METHYL ETHYL KETONE

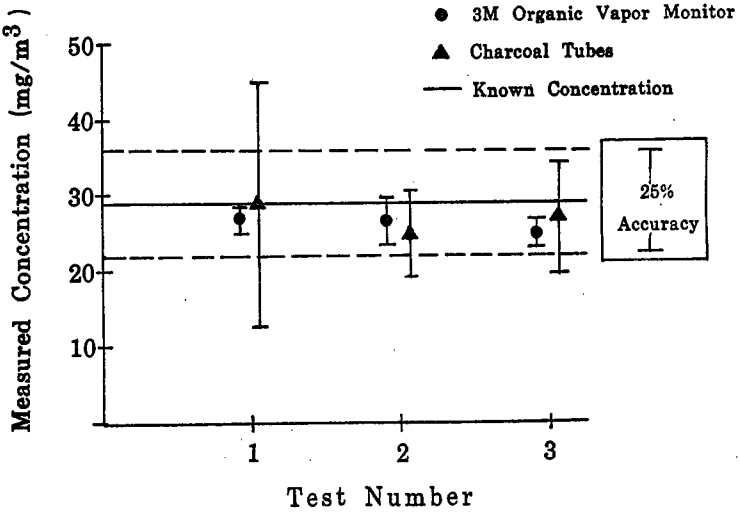


3M 110872

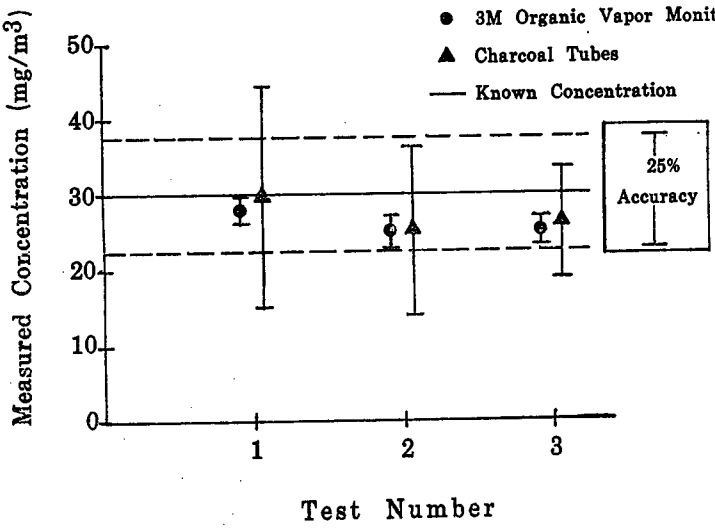

BENZENE
3M Organic Vapor Monitor
Charcoal Tubes
Known Concentration
25% Accuracy
Measured Concentration (mg/m3)
10
9
8
7
6
5
4
3
2
1
1
2
3
Test Number

3M 110873

TOLUENE

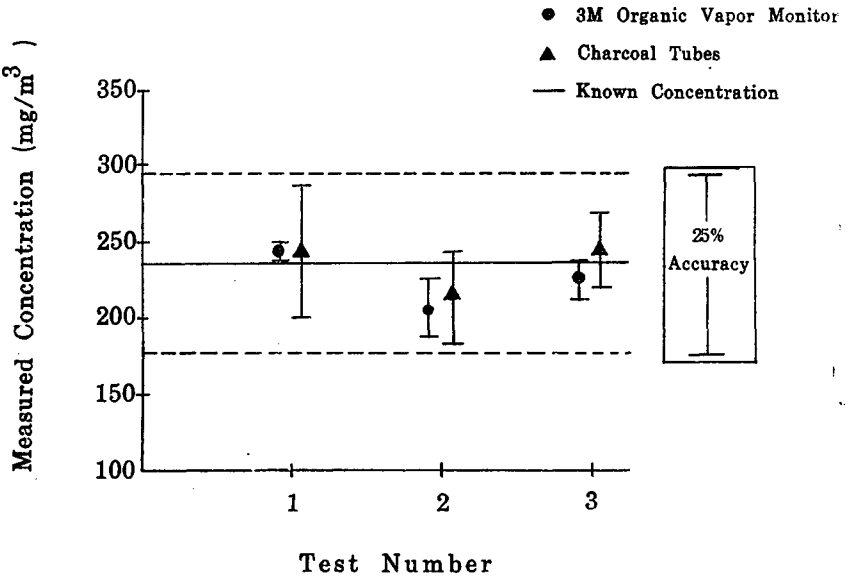


XYLENE



3M 110875

NAPHTHA (VM & P)



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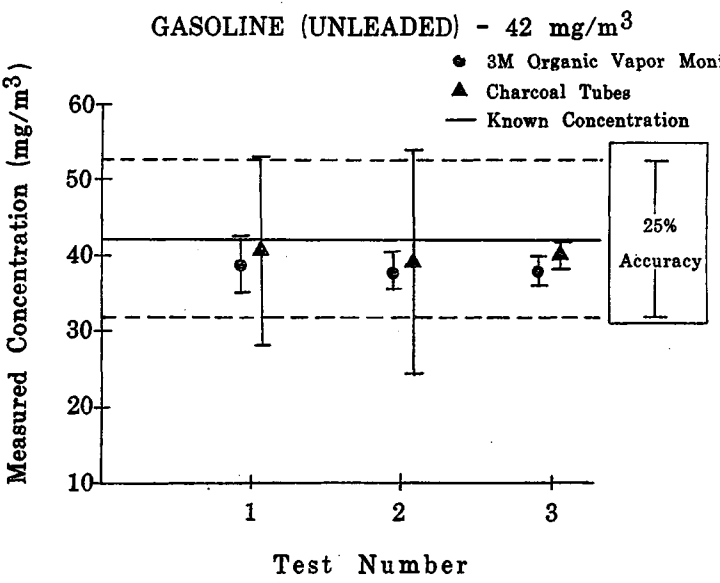
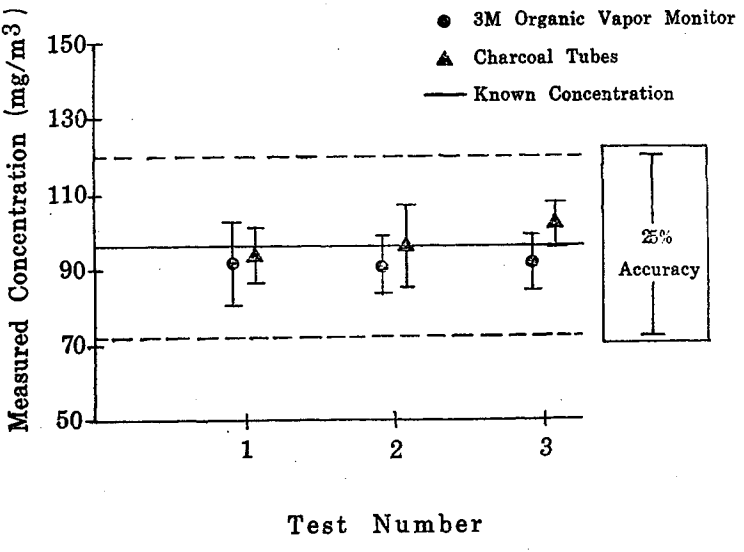
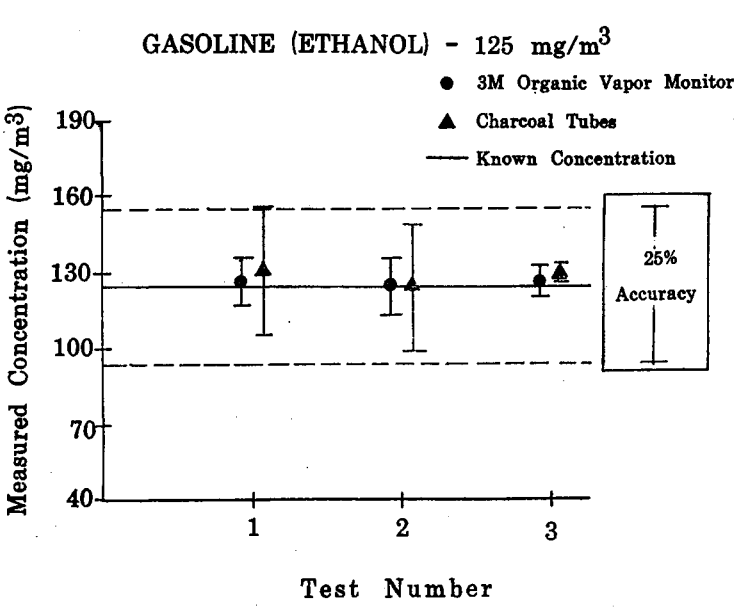
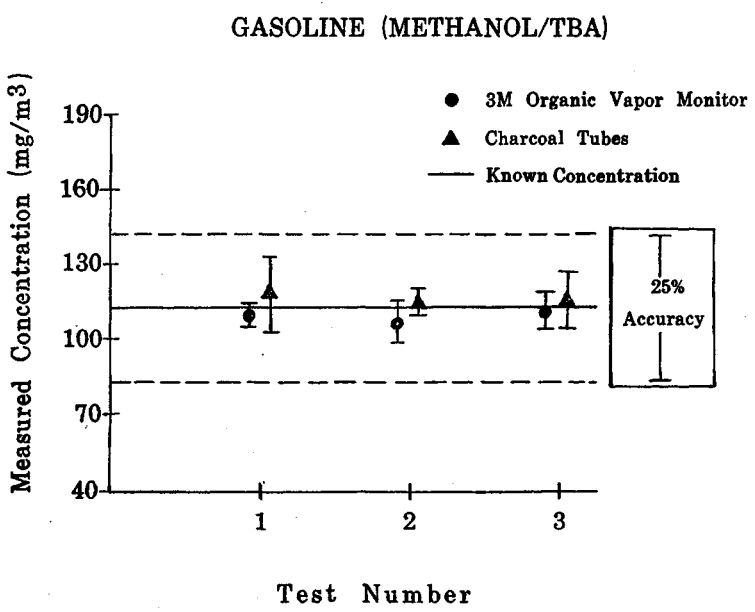

GASOLINE (UNLEADED) - 42 mg/m3
3M Organic Vapor Monitor
Charcoal Tubes
Known Concentration
Measured Concentration (mg/m3)
60
50
40
30
20
10
25%
Accuracy
1
2
3
Test Number

GASOLINE (UNLEADED) - 96 mg/m^3

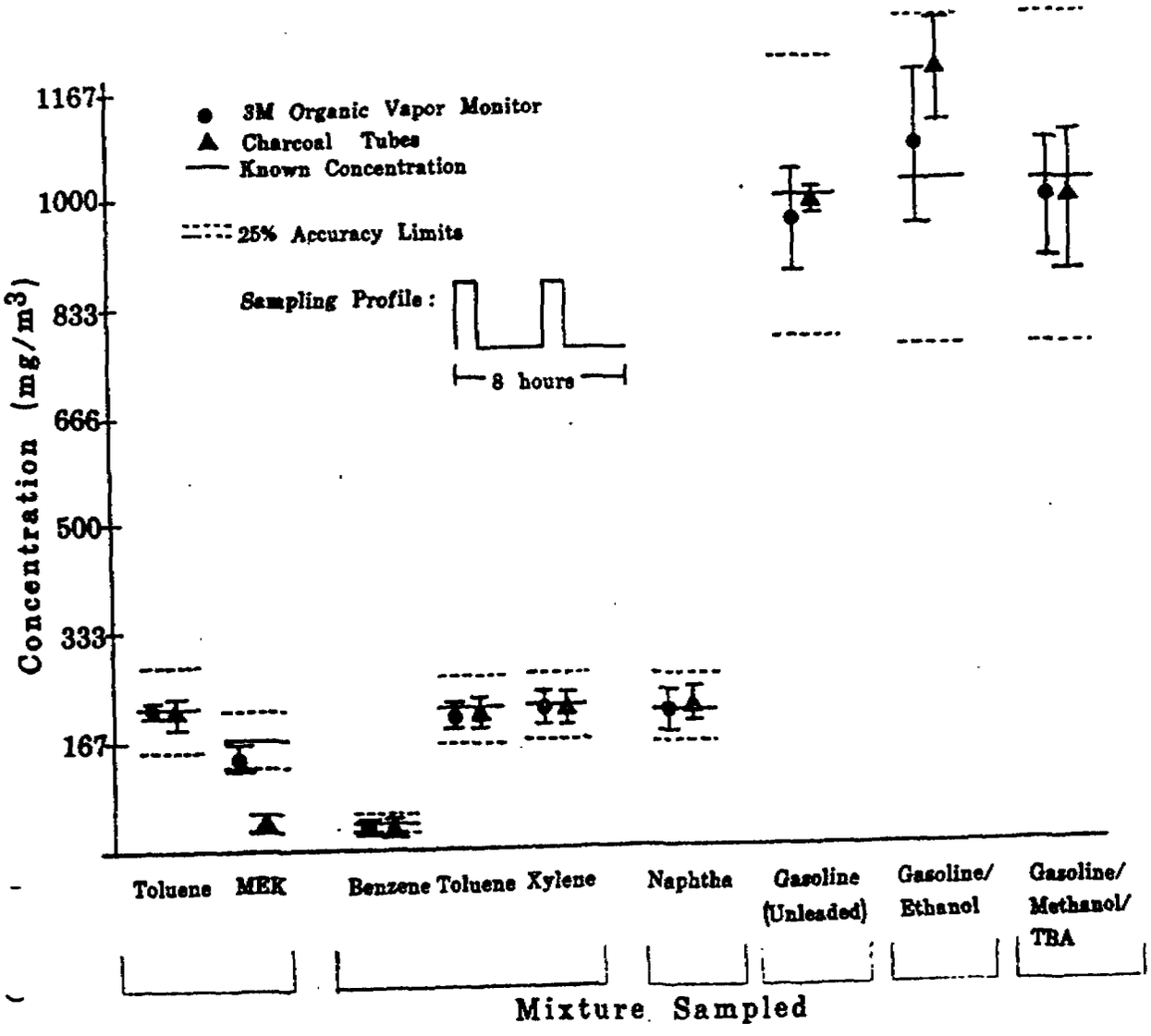


3M 110878

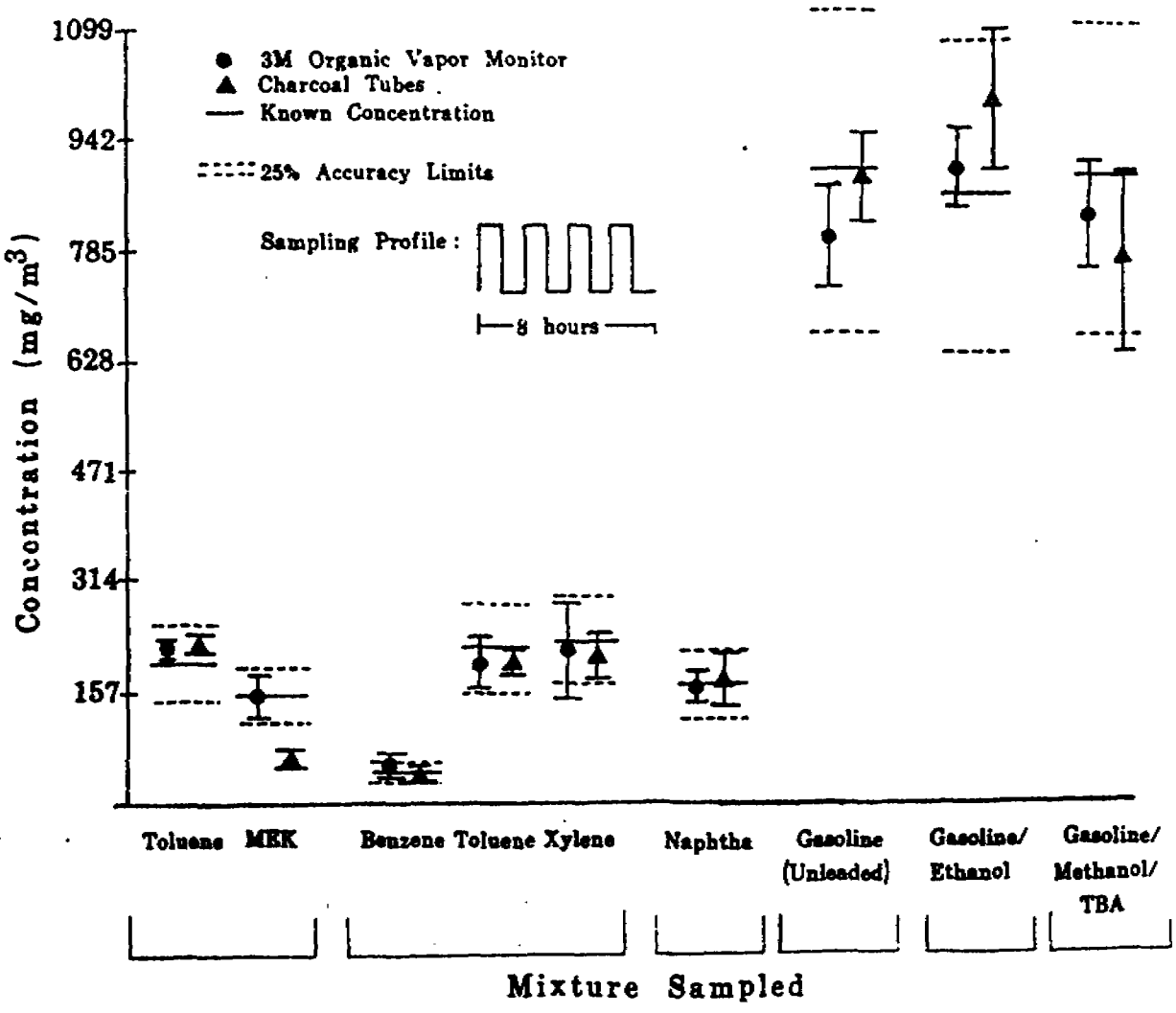

GASOLINE (ETHANOL) - 125 mg/m3
3M Organic Vapor Monitor
Charcoal Tubes
Known Concentration
Measured Concentration (mg/m3)
190
160
130
100
70
40
25%
Accuracy
1
2
3
Test Number


GASOLINE (METHANOL/TBA)
3M Organic Vapor Monitor
Charcoal Tubes
Known Concentration
Measured Concentration (mg/m3)
190
160
130
100
70
40
25%
Accuracy
1
2
3
Test Number

RESPONSE TO VARIABLE CONCENTRATION



RESPONSE TO VARIABLE CONCENTRATION



Waste anesthetic gas exposures present a possible health hazard to selected health professionals (surgeons, dentists, nurses, veterinarians, etc.) Effective control of these exposures depends upon an anesthesiologist or nurse implemented scavenging system for the anesthesia environment together with a routine monitoring system for exposed personnel. Personal charcoal tube samplers using battery-powered pumps require trained personnel to obtain valid results and are not compatible with mobility and sterility requirements of operating rooms. Continuous air monitors (*i.e.*, infra-red analyzers) are expensive and complicated to use. Alternatively, passive personal samplers developed to collect integrated time weighted average samples of gases in the worker breathing zone may be ideally suited for sampling the exposure in the operating room environment. This study investigates the performance of passive personal samplers at concentrations of anesthetic gases in the range of those found in operating rooms (5-20 ppm). A unique quasi-dynamic system was employed to maintain stable gas concentrations. Results obtained using the passive personal samplers were compared to charcoal tube samples and infra-red analyzer readings. Data indicate that passive personal samplers are capable of determining concentrations of enflurane with accuracies that range between ±24% to ±70%.

Laboratory performance of passive personal samplers for waste anesthetic gas (enflurane) concentrations

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Introduction

It has been clearly shown[1] that operating room and dental personnel are chronically exposed to varying concentrations of waste anesthetic gases. These gases, which include nitrous oxide with or without various volatile halogenated anesthetic agents, exist (in the uncontrolled workplace) at concentrations up to 1000 ppm.[2] Investigators have attempted to quantify the health sequelae of such exposures through a number of animal and human studies. Most reports conclude that occupational exposure to waste anesthetic gases may result in an increased risk of miscarriage, congenital anomaly, cancer, renal and hepatic disease and other overt health effects, plus decrements in psychomotor performance. Therefore, it has been concluded[3-5] that workplace levels of waste anesthetic gases should be controlled and that monitoring of worker exposures should become an important facet of the hospital regimen.

Monitoring waste anesthetic gas exposures may be done by several means. NIOSH recommends[2] that samples be analyzed by infra-red spectrophotometry or by gas chromatographic analysis of charcoal tube samples collected using sampling pumps. The former method relies upon a trained professional using a complicated and expensive machine to make measurements. The latter method requires the use of cumbersome pumps to take samples and often requires an individual to monitor flow rates, sampling times and placement. A viable alternative to conventional methods of sampling is the use of passive personal samplers. These samplers require no pumps and cannot break down, they are inexpensive, lightweight and easy to use. Two types of passive personal samplers have been described, differing in the type of molecular principle which they employ.

Permeation-type personal monitors[6] are passive samplers with polymeric membranes. Gases and vapors are absorbed in the membrane and permeate the membrane to be collected and stabilized in a medium such as charcoal. The transport of the gas in the sampler is represented mathematically by:

$$C = wk \cdot t \qquad (1)$$

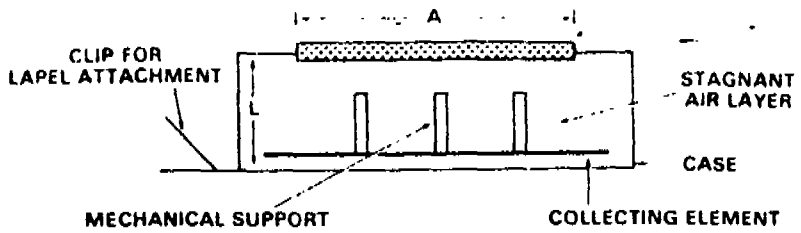
where C = concentration, ppm,
w = weight of contaminant, μg,
t = exposure time, hrs, and
k = permeation constant.

Permeation is limited by the diffusion through the membrane. The permeation constant is determined experimentally for the specific membrane used and the substance comprising the exposure. Use of a permeation-type passive sampler for monitoring vinyl chloride monomer has been described.[6]

The other type of passive sampler[7-11] operates on the principle of diffusion through a stagnant gas layer. Diffusional samplers are based upon movement of molecules through a draft-minimizing barrier to a collecting medium of large adsorptive capacity. Transport of a gas or vapor is based upon Fick's First Law of Diffusion:

$$J = \frac{DA(C_1 - C_2)}{l} \qquad (2)$$

where J = mass transfer rate, moles/sec,



A: CROSS SECTIONAL AREA, CM^2
L: PATH LENGTH, CM

Figure 1 – Typical diffusional sampler.

D = diffusion coefficient, cm^2/sec,
A = area of diffusional path, cm^2,
$C_i - C_o$ = concentration gradient, with C_i being ambient concentration and C_o being concentration at the collector surface, and
L = diffusional pathlength, cm.

Because of the large adsorptive capacity of the collecting material, C_o for the collecting material can be assumed to be zero. This makes the mass transfer rate proportional to the ambient temperature. Multiplying both sides by time, we get:

$$t \times \text{mass transfer} = t \times \text{collection rate, or}$$

$$\text{total mass} = DACt/L. \quad (3)$$

Due to the stagnant air layer in the sampler, transport is limited by Brownian motion. The driving force is therefore the concentration gradient difference between the ambient concentration C_i and the collecting medium concentration C_o. Thus a stagnant air layer between the draft shield and the collecting element is essential to prevent disturbance of the molecular processes.

A typical diffusional sampler is shown in Figure 1. Diffusional samplers which have been described differ mainly in diffusional geometry (A & L), types of housings and matrix in which the charcoal is presented. The Abcor Gasbadge[1M] is a large housing with replaceable charcoal elements, whereas the products made by 3M and DuPont are intended for single use. The 3M Organic Vapor Monitor is made for in-badge desorption with subsequent decanting of the fluid into vials for analysis or for straight injection into a gas chromatograph. The DuPont Pro-tek[1M] allows for high-flow and low-flow sampling by providing two removable covers (increases A two times when both covers are removed).

Two factors have been identified[12] as having the greatest effect on diffusion rate. The first factor is air velocity, and this relates to the driving force in equation 2, $C_i - C_o$. Equation 2 assumes that the ambient concentration is the same as C_i. This would be true for a situation with adequate convection. But when convection is minimum, *i.e.*, when V 0, $C_i - C_{ambient}$. In this case, where there is no convection, some of the resistance to transport previously described as residing in the internal stagnant air layer of the badge would be external to the badge, *i.e.*, a stagnant air layer outside the badge. Thus, where there is little convection, resistance to transport increases, and the weight of the vapor collected by the badge is no longer related to the concentration of vapor in the area. It has been shown[12] that at a face velocity below 15 ft/min, the dosimeter loses accuracy due to the increased convective resistance. Since ambient air velocities are usually a minimum of 50-75 ft. min, this is rarely a problem.

Temperature has also been identified as having a large effect on diffusion rate. The temperature dependance of the diffusion rate at ambient temperatures has been calculated[12] to be less than 0.2% °C. Thus a temperature change from 25 °C to 30 °C should change the diffusion rate by less than 1%.

This study is intended to examine three commercially available passive personal samplers in terms of their use in monitoring laboratory concentrations of enflurane. Enflurane was chosen for the study for several reasons. First, it is an anesthetic agent which is becoming widespread in hospital settings. It has a reputation for fewer toxicological effects associated with its use and thus is expected to replace halothane as the most widely used halogenated anesthetic in this country. Secondly, there is a dearth of information about monitoring for enflurane using these types of samplers (let alone using these samplers for monitoring any substance). Lastly, it is hoped that eventually field studies could be carried out in the operating rooms of a hospital to evaluate the field efficacy of using such a system for monitoring exposures. It would be quite helpful to have preliminary information concerning the functioning of these passive personal samplers in a controlled environment.

apparatus and procedures

A 379 liter (100 gallon) polypropylene cylindrical tank was adapted for use as an exposure chamber. One-half inch sampling ports were drilled in the side of the tank to allow for continuous sampling of the air with a MIRAN 1 A Portable Infra-red Gas Analyzer and concurrent charcoal tube sampling. To compensate for volume changes as a result of charcoal tube sampling, a 30 liter Mylar bag was

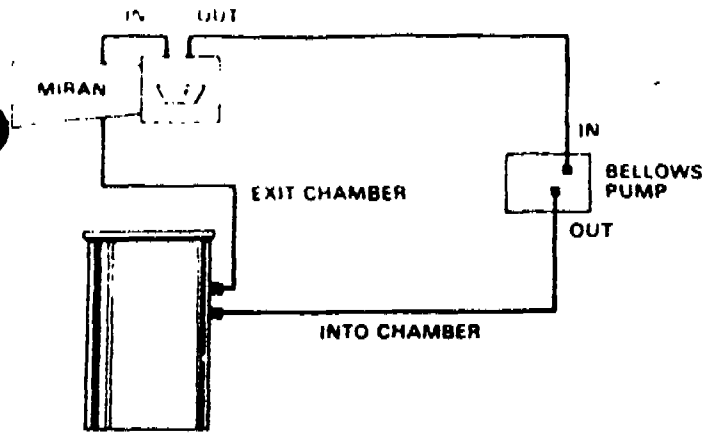


Figure 2 - Equipment set-up.

placed inside the chamber, with a Tygon tube acting as a vent to the outside air through the chamber's wall.

To maintain adequate air velocities across the samplers, a quasi-dynamic air flow system was utilized.[11] This system consisted of a Dayton blower which was connected to a reducer and then to an eight-inch duct. Badges were hung in the center at a distance of two diameters down the duct from the inlet by means of a wire support. This dimension was chosen as an area of minimum turbulence and maximum flow stability. The entire system was placed within the chamber.

Two one-eighth inch holes were drilled at right angles at a length down the duct equal to two diameters. Using an Alnor Type 8500 Thermo Anemometer, a traverse was taken to verify that velocities exceeded those required to minimize resistance to diffusional transport.

A one-half inch hole was drilled in the lid of the chamber, through which a thermometer was inserted. Thus, the temperature of the inside of the chamber was recorded during the course of an experiment.

Preparations to test samplers were as follows. Two samplers were clamped onto the wire support and lowered into the duct. The blower was turned on. The heavy polypropylene lid was placed in the tank and sealed around the top with pliable weather stripping. The access to the diaphragm (Mylar bag) was clamped and all other ports were shut off, save one port. A Gast pump was connected by a T to the chamber at this port and a manometer was connected to the other arm of the T. The vacuum pump was then turned on. The chamber was considered to be suitably sealed if the drop in the manometer (with 3 in. of vacuum and hose to the pump clamped) was less than 1/2 in./30 sec.

MIRAN 1-A

A MIRAN 1-A Portable Infra-red Gas Analyzer was utilized to monitor the concentration inside the chamber continuously. Operation and calibration of the analyzer were performed according to manufacturer's instructions. Comparison of the calibration curves for enflurane performed prior to a series of experiments was made with manufacturer's (Foxboro/Wilks) printed information.

Prior to each experiment, the infra-red analyzer was allowed to warm up for approximately 10 minutes. The MIRAN was hooked up in series with the chamber as depicted in Figure 2. The sample size calculated to give the appropriate chamber concentration was injected into the bellows pump, and the experiment was begun at that point. Thereafter, a sample was drawn through a charcoal tube the first fifteen minutes out of every hour for the six hours of the experiment (for sampler A) or for two hours during the third and fourth hours of the experiment (for samplers B and C). A DuPont low flow pump was used to draw samplers through SKC charcoal tubes. The pump was calibrated using a bubble meter and was run off house power via the battery charger.

TABLE I
Summary of Data[1]

Sampler		Amount Adsorbed μL[2]	Tank Concentration ppm[3]	MIRAN Concentration ppm[4]	Charcoal Tube Concentration ppm[5]
Dupont	A	1.89	20	16.5	18.3
		.85	10	9.2	7.9
		.26	5	4.7	3.9
3M-OVM	B	.78	20	15 8	19.8
		.36	10	8.2	9.3
		.79	5	4.3	4.9
Gasbadge	C	.77	20	16 4	18 1
		.62	10	9 2	12.7
		.35	5	3 9	7.0

[1] Obtained by averaging raw data for each group of runs.

[2] This represents the total amount of enflurane adsorbed by the sampler, obtained by comparing gas chromatographic analysis of the samples against a standard curve for enflurane

[3] Determined using the amount injected into the chamber, and adjusting for chamber volume.

[4] Determined by averaging fifteen minute interval readings of adsorbance at wavelength 8 7 μm and comparing against a standard curve for enflurane.

[5] Determined as above for the sampler, only the μL of sample w as converted using sp gr. to mg and divided by the sample volume to yield ppm

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TABLE II
Regression Analysis of All Combinations of Four Variables

PPS	Regression	Correlation	Intercept	Slope
A	BADAD with TANKON	.834	.238 μL	.107 μL ppm
	BADAD with CHRCOL[a]	.806	.085 μL	.095 μL ppm
	BADAD with MIRAN[b]	.846	.434 μL	.140 μL ppm
	CHRCOL with TANKON[c]	.925	.177 ppm	.998 ppm ppm
	MIRAN with TANKON[d]	.996	1.08 ppm	.778 ppm/ppm
	MIRAN with CHRCOL[e]	.934	3.58 ppm	.667 ppm/ppm
B	BADAD with TANKON	.960	-.024 μL	.040 μL/ppm
	BADAD with CHRCOL	.970	-.012 μL	.040 μL/ppm
	BADAD with MIRAN	.963	-.050 μL	.052 μL/ppm
	CHRCOL with TANKON	.994	-.338 ppm	1.00 ppm/ppm
	MIRAN with TANKON	.998	.494 ppm	.764 ppm/ppm
	MIRAN with CHRCOL	.996	.821 ppm	.758 ppm/ppm
C	BADAD with TANKON	.730	.275 μL	.026 μL/ppm
	BADAD with CHRCOL	.830	.079 μL	.038 μL/ppm
	BADAD with MIRAN	.748	.259 μL	.033 μL/ppm
	CHRCOL with TANKON	.898	4.48 ppm	.707 ppm/ppm
	MIRAN with TANKON	.993	.422 ppm	.813 ppm/ppm
	MIRAN with CHRCOL	.917	-2.22 ppm	.949 ppm/ppm

[a]Regression of badge-adsorbed sample on tank concentration (from amount injected into chamber and volume of chamber).

[b]Regression of badge-adsorbed sample on charcoal tube concentration.

[c]Regression of badge-adsorbed sample on MIRAN concentration.

[d]Regression of ppm's using charcoal tubes on/tank concentration.

[e]Regression of MIRAN concentration on tank concentration.

[f]Regression of MIRAN concentration on charcoal tube concentration

TABLE III
Regression Analysis-Fit Through Zero

PPS	Regression	Correlation	Multiple R-Square[a]	Slope
A	BADAD with TANKON	.955	.921 μL	.092 μL/ppm
	BADAD with CHRCOL	.950	.093 μL	.101 μL/ppm
	BADAD with MIRAN	.954	.910 μL	.108 μL/ppm
	CHRCOL with TANKON	.983	965 ppm	.888 ppm/ppm
	MIRAN with TANKON	.998	.997 ppm	.847 ppm/ppm
	MIRAN with CHRCOL	.981	.963 ppm	.922 ppm/ppm
B	BADAD with TANKON	.990	981 μL	.039 μL/ppm
	BADAD with CHRCOL	.993	986 μL	.039 μL/ppm
	BADAD with MIRAN	.990	.981 μL	.049 μL/ppm
	CHRCOL with TANKON	.999	997 ppm	.979 ppm/ppm
	MIRAN with TANKON	999	.999 ppm	.795 ppm/ppm
	MIRAN with CHRCOL	.999	.998 ppm	.810 ppm/ppm
C	BADAD with TANKON	.947	.896 μL	.044 μL/ppm
	BADAD with CHRCOL	.979	958 μL	.044 μL/ppm
	BADAD with MIRAN	.952	.906 μL	.053 μL/ppm
	CHRCOL with TANKON	.975	.951 ppm	1.02 ppm/ppm
	MIRAN with TANKON	.998	.997 ppm	.833 ppm/ppm
	MIRAN with CHRCOL	982	964 ppm	.784 ppm/ppm

[a]Square of the regression (correlation).

MIRAN-assessed concentration in the chamber was determined by dividing the chart into fifteen-minute periods and obtaining the absorbance (at 8.7 μm) for each period. The average absorbance was taken as the sum of the fifteen-minute absorbances divided by 25, and the concentration was obtained from the calibration curve.

After each run, weather stripping was removed from around the top of the chamber. The passive samplers were either sealed in packages, or the elements were transferred to vials. Charcoal tubes were capped. All samples were refrigerated until analysis was performed.

TABLE IV
Calculated Diffusion Coefficients

Source	D, cm²/sec
PPS A	129
PPS B	076
PPS-C	144
M[1]	076
LAJ[2]	056
X	076

[1]Calculated using reported sampling rates.[14] Since Sampling rate = DA/L, by dividing reported rate for enflurane of 26.1 cm³/min, by A/L × 60, obtain D.

[2]Based on equation relating diffusion coefficient to molecular weight:[15]
$\log D = 0.3927 - 0.7238 \log W$
where log = $\log_{10}$
D = Diffusion coefficient cm²/sec, end
MW = Molecular weight, g/mole.

µs chromatographic analysis

Analysis on samples was performed at the Maryland Department of Health and Mental Hygiene, Occupational Health and Air Quality Laboratory, an American Industrial Hygiene Association accredited laboratory. Methods of Analysis were as recommended by NIOSH. Abcor samples were desorbed in three mL of carbon disulfide, 3M samples were desorbed in two mL and one mL was used to desorb the DuPont samples and charcoal tubes. Samples were placed on a laboratory shaker for 30 minutes prior to analysis on a Varian 2445 gas chromatograph with auto sampler and FID detector.

Chromatographic conditions were:

1/8 in., 20 ft. stainless steel 10% FFAP on Chromosorb W, 60-80 mesh column
Column temperature: 60 °C
Injection temperature: 210 °C
Detector temperature: 230 °C
Carrier gas: N_2, 25 mL/min
H_2: 25 mL/min
Air: 300 mL/min to FID

desorption efficiency

The desorption efficiency for each of the three passive personal samplers was determined experimentally. Sampling elements were placed into sealable containers and µL, 2 µL, or 3 µL of liquid enflurane was carefully added to the charcoal. The samples were allowed to equilibrate for 24 hours. The samples were desorbed as usual (described above). The desorbed samples were analyzed for enflurane chromatographically (see above) and the amount of enflurane in the desorbing fluid (µL enflurane) was calculated from standard curves. Desorption efficiency was defined as the amount of enflurane recovered in desorbing fluid divided by the amount of enflurane to which the badge was exposed. Values greater than 1.0 indicated some discrepancy in ascertainment.

results

For the purposes of this study, passive personal samplers were relabeled A, B and C. Table I summarizes the grouped data for all experiments. To facilitate data analysis, variable names were given for the different sample concentrations: BADAD, for amount adsorbed on the sampler; TANKON, for the calculated amount in the chamber, based on injection volume; MIRAN, for concentration determined using infrared analyzer; and CHRCOL, for concentration determined by charcoal tube samples.

Table II shows the results of regression analysis on all data. In this table and subsequent tables of regression, "BADAD with TANKON" indicates the regression analysis of independent variable TANKON with dependent variable BADAD. Similarly, regression analysis was re-run in Table III utilizing a computer program that fit the line through the origin.

discussion

reproducibility

This study compared four different methods of assessing the levels of an anesthetic vapor in a test chamber. Any method can be used profitably if an understanding of the sensitivity, accuracy and precision of the methods exists. Since these tests involved a rather narrow range of exposure concentrations, sensitivity of each method may not be determined, but the reliability with which a method discerns accurately the concentration of gas to which it is exposed can be determined by repeated measurements of similar concentrations.

From Table I it can be seen that tank concentration does not vary within each concentration level. This is a result of calculating the amount of enflurane needed to create a test atmosphere of the desired concentration, using the tank volume and specific gravity of the substance. The amount of enflurane was injected into the chamber at the beginning of an experiment. Any variation in tank concentration will not be discernable since there is no check on the amount actually delivered from the Hamilton syringe to the bellows pump nor the amount which vaporized immediately, nor the amount which was lost by adherence to walls of the chamber. If one assumes that the last two factors exert negligible effect on tank concentration, then any variation in tank concentration will be a function of the accuracy with which one can deliver an aliquot of volatile liquid using a 50 µL Hamilton syringe which is then the primary standard. It is estimated, therefore, that this accuracy is ± 1 µL or ± 0.48 ppm for this exposure chamber. Of the four methods, tank concentration is believed to have the least amount of error associated with it; this justifies its use as the primary standard for concentration measurement in this study.

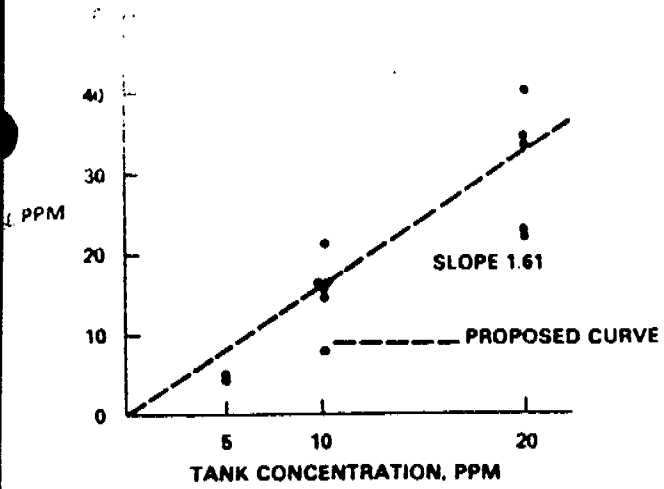

Figure 3 – Badge versus tank concentration - Sampler A.

Regression analysis was performed assuming a linear regression model. It was believed that a linear model was appropriate since response on charcoal is assumed to be linear below the loading capacity of the collecting element. Since the loading capacity of the badges is estimated to be around 10-15 mg, and the badges only adsorbed at the most 3 μL × 1.50 mg/μL = 4.44 mg, the assumption appears to be reasonable.

Regression analysis showed high correlation with all variables tested. MIRAN with TANKON shows the highest correlation in all three samplers, which indicates uniformly high accuracy in all experiments using the MIRAN, when compared to the designated primary standard. Correlation indicates how much the dependent variables deviate from the calculated regression line. Where BADAD was the dependent variable, sampler B consistently had the highest correlations, followed by A and then C. The high correlations were seen when BADAD was regressed on MIRAN. This may reflect the [illegible] MIRAN concentration since two badge data points were obtained for one MIRAN data point. MIRAN with TANKON consistently shows highest correlation.

It was observed that in many of the regressions the intercept was non-zero. Since all blanks were seen to be zero this can be attributable to random errors in methods for determination of enflurane concentration. In Table III regression analysis was repeated, but the regression lines were fitted through zero. All correlations were seen to increase, but sampler B still has the highest correlation when BADAD is regressed on TANKON (.990), with sampler A next highest (.955) and sampler C last (.947). It is difficult to see how much difference this makes in the arrangement of the data since all three correlations are very close to one. BADAD regressed on TANKON graphically for samplers A, B and C (figures not presented) show that the greatest deviation of the points from the line is in sampler C; in fact, it appears that the regression line for sampler C may be more appropriately curvilinear. Sampler B shows the best fit to the linear regression model with all points close to the regression line.

diffusion coefficient

In order to convert from weight of gas collected by the badge to ppm, it is necessary to know the diffusion coefficient of the gas in air. In this way:

$$mg/m^3 = \frac{G.W.}{(D.E.)(A/L)(D)(S.T.)} \quad (4)$$

where G.W. = weight of gas collected by sampler, ng,
D.E. = desorption efficiency,
A/L = sampler geometry or ratio of cross-sectional area to length, cm,
D = diffusion coefficient, cm^2/sec, and
S.T. = sampling time, sec.

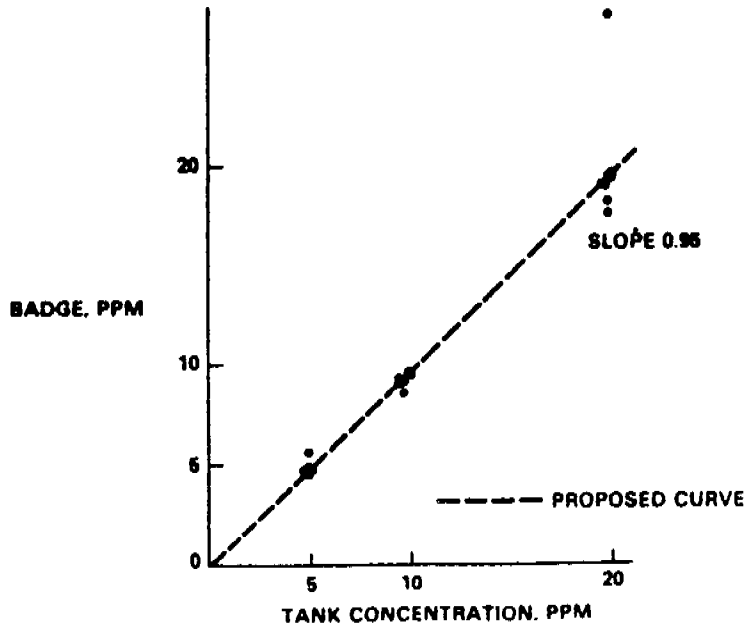

Figure 4 Badge versus tank concentration Sampler B

From this it can be shown that

$$ppm = mg\ m^{-3} \times \frac{22.4\ l\ mole}{M.W.\ g\ mole} \times \frac{T\ K}{273\ ^{\circ}K} \times \frac{760\ mm\ Hg}{P\ mm\ Hg} \quad (5)$$

Since this study was done at 1 atmosphere and at approximately 25° C, this becomes

$$ppm = mg\ m^{-3} \times \frac{24.45\ L\ mole}{M.W.\ g\ mole} \quad (6)$$

The diffusion coefficient, shown in equation 4 to be necessary to convert weight of gas on the badge to ppm, is provided for many solvents by the sampler manufacturers. The constant D is not generally given; what is typically given is the sampling rate, or DA/L. However, if one knows the sampling rate of a sampler for benzene, for example, one can divide through by the published diffusion coefficient for benzene to obtain A/L, the diffusional geometry of the sampler. This was done for all three samplers for the conditions of use, such that $A_{A\,L} = 7.34$ cm, $B_{A\,L} = 5.90$ cm and $C_{A\,L} = 7.67$ cm. Using these values, and graphical representations of μL adsorbed by badge versus tank concentration in ppm using slopes obtained by regression analysis (Table III), the diffusion coefficient was back calculated by the following method. For each badge, 1 μL could be found to correspond to x ppm. Since μL can easily be converted to mg using data on specific gravity, substituting into equation 6, and then equation 4 allowed for deduction of the diffusion coefficient as implied by each badge. Desorption efficiency of each badge was included in the calculation, with samplers A, B and C giving D.E.'s of .90, .81 and 1.17 respectively. Analytical error is believed to have a large part in the anomalous results of D.E. for sampler C.

The results of the above calculations are presented in Table IV. Included in this table is a diffusion coefficient calculated from a published sampling rate.[4] Another estimate of the diffusion coefficient for enflurane is an equation in which log D is related to the log of the molecular weight. The average of all five values for D is .076 cm^2/sec.

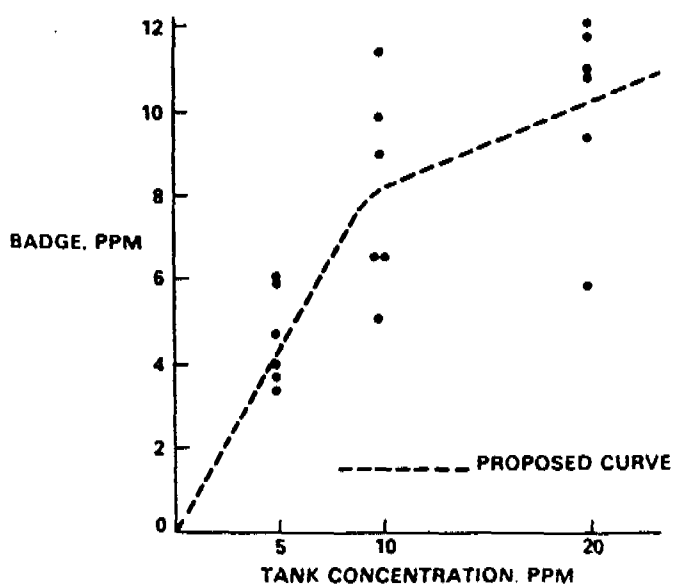

Figure 5 Badge versus tank concentration - Sampler C.

TABLE V
Coefficients of Variation

Tank Concentration ppm	PPS A	PPS-B	PPS-C	MIRAN	Charcoal
5	09	.08	24	10	11
10	28	06	.30	07	27
20	34	16	.23	03	25
C.V., overall	30	12	35	08	23

[1]Calculated by taking the sum of the observed concentration divided by the tank concentration, taking the standard deviation of the sum and dividing by the mean.

This appears to be the best approximation. It is further gratifying that the diffusion coefficients from PPS-B and M are the same, since the samplers were the same in both studies.

Once the diffusion coefficient for enflurane is obtained, it becomes a simple matter to convert μL enflurane collected by each badge to ppm. Graphical representations of badge concentration were made and are presented in Figures 3, 4 and 5. These representations show that sampler A overestimates tank concentration by about 60%, while sampler B underestimates tank concentration by about 5%. Sampler C appears not to be a linear relationship at all when plotted as seen by the scatter of the points away from the best fit curve.

coefficient of variation

It has been written[16] that "the relative variation of a normal distribution (such as randomly distributed errors occurring in industrial hygiene sampling and analytical procedures) is commonly described by the coefficient of variation (CV) . . . The CV is a useful index of dispersion in that limits computed from the true mean of a set of data plus or minus twice the CV will contain 95% of the data measurement." CV's were thus computed in order to gauge the accuracy of the methods used to determine the concentration in the tank. In this case, accuracy is defined as "the difference between a measured concentration and the true concentration of the sample . . . it includes both the random variation of the method about its own mean (commonly referred to as precision) and the difference between the average result from the method and the true value (commonly referred to as the bias of the method)".

CV's were calculated by taking the observed value dividing by the tank concentration (O/E), computing the standard deviation, and dividing by the mean. CV's were determined over all data points within a method, and within a tank concentration level. Table V presents a summary of the calculated coefficients of variation for the three badges tested and for the MIRAN and charcoal tube measurements. The lowest overall CV's were observed for the MIRAN and PPS-B, with CV's of 8% and 12 respectively. The charcoal tube coefficient of variation was 23% overall; this is twice as high as the published CV of

[illegible] has not been collaboratively tested for [illegible]. With PPS-A, a low CV was seen at the lowest concentration. It seems the CV for PPS-A changes from .09 ppm to CV = 34% at 20 ppm. The source of this [illegible] is unknown. PPS-C is most notably the least accurate sampler tested, with an overall CV = 35%.

Velocity and temperature effects

From the velocity traverse taken in the exposure system, it is assumed that the boundary conditions of the transport equation were met, *i.e.*, velocity of the duct at each point in the duct exceeds the 15 ft/min necessary to measure concentration. At no place in the duct did the velocity measure less than 70 ft/min.

A slight rise in temperature (< 6 °C) was noted after a six-hour experiment. The temperature rise was attributed to the motors on the Dayton blower plus the bellows pump. Some heat gain may have been due to radiant heat gain, as the exposure system was stationed near a window. The heat rise of 5.6 °C should have a negligible effect on the diffusion experiments being performed, since (as discussed earlier) one would expect only about a 1% change in diffusion rate. Therefore, the temperature rise noted in the experiments is believed to have a negligible effect on the performance of the samplers.

conclusions and recommendations

Three commercially available passive personal samplers were examined experimentally in a controlled environment. They were compared against standard methods of sampling for enflurane. Large differences in accuracy were discovered in the samplers and two parameters (temperature, velocity) associated with their use were examined and found to have little operator error associated with their use. However, the accuracy of the devices should be further evaluated in order that their reliability for the assessment of occupational and environmental exposures can be known in a variety of applications.

This study has suggested possible non-linearity in the performance of some passive personal samplers. It is hoped that this work will be elaborated on in further experiments of larger sample sizes and greater ranges of enflurane concentrations. Passive personal samplers hold great promise for the future of industrial hygiene sampling and analysis, but only with extensive testing of the devices.

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Seventy eight pairs of side-by-side charcoal tube and 3M Brand '' passive vapor monitor samples were taken in the field and analyzed for 22 rganic chemicals including trichloroethylene, benzene, toluene, MEK, m-, p-, and ylenes, isopropanol, and several C5 through C8 alkanes. Sixty-four pairs were personal and fourteen pairs re area samples Linear regression analyses were performed for ten ch micals detected over a sufficiently large range of concentrations. Satisfactory correlation (r · 0.90 and slopes not significantly different from 1.0) was found between monitors and tubes for n-hexane, methylcyclopentane, toluene, 2-methylpentane, 3-methylpentane, n-heptane, n-pentane, and isopentane. Tube and monitor results differed for methylcyclohexane and n-octane. Paired t-tests were performed on the remainder of the chemicals, and no consistent significant differences (5% level) in the means were found.

Field comparison of charcoal tubes and passive vapor monitors with mixed organic vapors

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introduction

Several brands of charcoal-adsorption passive vapor monitors have been marketed recently. These monitors hold much attraction for measuring workplace vapor exposures because they are lightweight, require no power, pump, or tubing, and are not likely to interfere with workers' movements.

The operating principles of these monitors have been described, and their advantages and limitations have been compared to those of charcoal tube pump monitoring systems.[1-3] The performance of passive monitors has been evaluated for various chemicals under various conditions.[4-6]

However, field studies of the performance of passive monitors in assaying mixed organic vapors are lacking, although an extensive field comparison of passive monitors and charcoal tubes is planned.[7]

procedures

Seventy-eight sets of simultaneous charcoal tube and 3M Brand #3500 organic vapor monitor samples were collected and analyzed for 22 organic chemicals as part of a survey of tire manufacturing facilities. The chemicals, listed in Table I, were selected for analysis on the basis of their presence in materials used in tire manufacture.

Samples were collected during regular work shifts in two plants during two 2-day periods in July and August, 1979. Sixty-four sets were personal samples and 14 were area samples.

The sampling periods varied from three to five hours. Charcoal tubes were usually changed during the sampling riod to reduce the possibility of overloading; the monitors ere not. Thus, with few exceptions, each pair of results consists of the concentration from a single monitor and the time weighted average concentration from two charcoal tubes.

chemical analysis

After exposure to the solvent vapors, the organic vapor monitors and charcoal tubes were capped and stored at -7°C until time of analysis. Monitors were analyzed in accordance with the manufacturer's instructions,[3] using a Perkin-Elmer gas chromatograph (Model Sigma 1) equipped with a flame ionization detector. Concentration data were calculated with a Perkin-Elmer Sigma 10 data system. The desorption efficiency for each solvent was determined by our laboratory using the method recommended by the 3M Company.[3] Concentrations were calculated in accordance with manufacturer's instructions.[3] The diffusion factors or "*sampling rates*" (analagous to diffusion coefficients) used are listed in Table I for each chemical. Charcoal tubes were desorbed in the standard manner and analyzed under the same procedures as the monitors.

results

Ten of the chemicals were detected over a sufficiently wide range of concentrations in one or both plants to permit a linear regression analysis of passive monitor and charcoal tube sampling results. Slopes, intercepts, correlation coefficients and 95% confidence intervals for prediction of individual values[8,9] are given in Table II, separately for the two surveys and for the combined data from both groups. Charcoal tubes were (X) values and monitors were (Y) values; that is, charcoal tube sample results were considered to reflect "*true*" concentrations, as a basis for comparison.

The second column in Table II indicates the range of concentrations found in the samples. Columns 3 and 4 are the slope and Y-intercept of the linear regression line, which indicates how well the two methods agree. A slope of 1.0 and at Y-intercept of zero indicate close overall agreement. The correlation coefficient (column 5) reflects the degree of

TABLE I
Chemicals Analyzed and Sampling Rates

Chemical	Sampling Rates (mL/min)*
Isopentane	29.8
n-Pentane	29.8
2,2-Dimethylbutane	28.2
3-Methylpentane	28.2
2-Methylpentane	28.2
n-Hexane	28.2
Cyclopentane	28.2
Methylcyclopentane	28.2
n-Heptane	27.7
Cyclohexane	28.2
Methylcyclohexane	27.2
n-Octane	21.8
1,1,1-Trichloroethane	28.1
Methyl ethyl ketone	31.2
Isopropanol	35.9
Benzene	33.0
Trichloroethylene	28.0
Toluene	30.4
Ethylene dichloride	32.1
p-Xylene	23.7
m-Xylene	25.6
o-Xylene	25.7

*Reference #6.

departure of data-pairs from the regression line. An r value of 1.00 indicates near perfect correlation, and lower r values indicate poorer correlation. The last two columns are the predicted 95% confidence limits of an individual passive monitor sample, given some "*true*" concentration of X as indicated by charcoal tube samples. The predictions were made for concentrations at the top of the data range observed.

The other twelve chemicals were detected in comparatively few samples or mostly at low concentrations (less than 1 ppm), so no linear regression analyses were performed. Instead, the paired t-test[7] was used to determine if the monitor and tube sample means were statistically different at the 0.05 probability level, assuming normal distribution. No consistent difference in means was demonstrated except for n-octane.

discussion

The data in Table II show two trends. In Group No. 1, for every chemical except n-heptane the passive monitors show higher vapor concentrations than the charcoal tubes, as indicated by linear regression slopes greater than 1.0. In three cases (toluene, n-octane and methylcyclohexane) the slopes were significantly different at the 95% confidence level from the ideal slope of 1.0. The observation of higher concentrations from passive monitors than from charcoal tubes is not unique. In one report,[10] acrylonitrile was monitored with 18 Gasbadges™ and charcoal tubes side-by-side; the badges averaged 2.73 ppm and the tubes 2.14 ppm, a mean difference of 25 percent.

The second trend was that Y-intercepts for nearly all chemicals in all groups were very close to zero (less than 1 ppm), and were in the main negative. Although a slight negative intercept is of little importance in monitoring substances with relatively large TLVs, it may indicate a detection threshold or lack of sensitivity in the passive monitors at very low concentrations. Such a condition, if confirmed, should be considered in making decisions on the use of passive monitors for detection of substances with TLVs in the 1 ppm range or lower.

Correlation coefficients (r) for several of the substances were 0.94 or higher. The 95 percent prediction limits on individual passive monitor sample concentrations are shown in Table II for given chemical concentrations. The predicted monitor concentrations are generally within ±25 percent of the reference concentrations, in Group No. 2 and the combined data, but vary widely in Group No. 1 because of the high slope values. This predictability would be much improved by use of the regression curve to "calibrate" the monitors. However, it is presumed that the curve will not be known *a priori*. If the slopes for any chemical had consistently varied from 1.0 appreciably in both groups (as with n-octane and methylcyclohexane), an inaccurate "*sampling rate*" for diffusion published by the passive monitor manufacturer might be responsible.

For the statistical analysis, charcoal tube sampling results were presumed to reflect the true concentrations, and be subject to much less variation than the passive monitors. This is by no means a certainty. However, statistical analyses where both methods are subject to error are rather complicated[11] and the method used here is considered to be satisfactory for this purpose.[12]

sources of error

Several possible sources of errors in the results of this study are discussed below.

1. The "sampling rates" used with the monitors may be imprecise. These sampling rates are analagous to diffusion coefficients. Published sampling rates were used where available; the others were estimated on the basis of chemical similarity. Use of too low a sampling rate would increase the slope (b) of the regression line in inverse proportion to the sampling rate error, but would not affect the correlation coefficient. This result was observed with methylcyclohexane, raising the possibility that the estimated "sampling rate" used (27.2 mL/min) was too low. Use of too high a sampling rate would tend to depress slopes in inverse proportion to the error. This type of systematic error could account for regression line slopes tending to be consistently greater than 1.0.
2. There may have been interference from unknown chemicals. Many small unidentified peaks were present in some of the chromatograms. Such interference would have affected tubes and monitors similarly.
3. On-site temperature and pressure departures from 298 °C and 760 mm were not corrected. They were presumed to affect monitors and tubes equally except for the temperature correction[2] to the sampling rate $(T°K/298)^{1.5}$. This could cause differences in monitor results ranging from -3 to +5 percent, as

TABLE II
Comparison of Results of Simultaneous Sampling by Passive Monitors and Charcoal Tubes

Chemical	Range of Data (ppm)	Linear Regression Slope & 95% C.L.	Y-Intercept (ppm)	Correlation Coefficient (r)	95% Prediction Interval for Passive Monitor Sample at True Concentration X: X (ppm)	Monitor Sample (ppm)
Group No. 1 (30 sample pairs)						
n-Hexane	0-37	1.02 ± 0 12	-0 50	0 96	40	33 8 to 46 6
Methylcyclopentane	0-17	1.11 ± 0 13	-0 72	0 96	20	18 3 to 24 6
Toluene	0-18	1 31 ± 0 12	-0 36	0.97	20	23 2 to 28 6
n-Octane	0-10	1 41 ± 0.15	0 01	0.96	10	12 0 to 16 2
2-Methylpentane	0-18	1 10 ± 0 15	-0.50	0.94	20	17 7 to 25 5
3-Methylpentane	0-30	1.13 ± 0 16	-0.61	0 94	30	27 0 to 39 5
n-Heptane	0-7	0 94 ± 0 13	-0.31	0.94	10	7.3 to 10 9
Methylcyclohexane	0 7	1.33 ± 0.30	-0 04	0.86	10	9.7 to 16.9
n-Pentane	0-6	1 29 ± 0 47	-0.01	0 73	10	7.9 to 17.9
Isopentane	0-13	1 12 ± 0 68	0.92	0.54	10	3.4 to 20 9
Group No. 2 (48 sample pairs)						
n-Hexane	0-27	0.91 ± 0 10	-0 11	0.94	25	17 9 to 27.6
Methylcyclopentane	0-20	0.99 ± 0.11	-0 26	0.94	20	16.1 to 22 9
Toluene	0-20	0 97 ± 0.10	0 16	0.97	20	16.6 to 22.4
2-Methylpentane	0-16*	0.92 ± 0 07	0.04	0 97	20	16.2 to 20.6
3-Methylpentane	0-30	0.91 ± 0 05	-0.02	0 98	30	24.6 to 30.0
n-Heptane	0-25*	1.09 ± 0 13	-0.56	0.93	25	22 2 to 31.0
Methylcyclohexane	0-20	1.39 ± 0.13	-0 15	0 96	20	24 3 to 31.0
n-Pentane	0-30*	0 93 ± 0.07	-0.05	0.97	30	24 1 to 31.3
Isopentane	0-40**	1.06 ± 0 03	-0.17	0 99	40	40.4 to 44.2
Combined Data (78 sample pairs)						
n-Hexane	0-37	0 97 ± 0.07	-0 26	0.95	40	33.5 to 43.9
Methylcyclopentane	0-20	1 03 ± 0.08	-0.38	0 95	20	17 6 to 23 6
Toluene	0-20	1.09 ± 0 08	0 06	0 95	20	19 0 to 24 6
2-Methylpentane	0-18	0.99 ± 0 07	-0 09	0 95	20	17 1 to 22.5
3-Methylpentane	0-30	1.01 ± 0 06	-0 15	0 97	30	26.4 to 33 8
n-Heptane	0-25	1 07 ± 0.10	-0 53	0 93	25	22.7 to 29.7
Methylcyclohexane	0-20	1.38 ± 0.11	-0 12	0.94	20	24.4 to 30.6
n-Pentane	0-30	0.92 ± 0 07	0 15	0 95	30	24 3 to 31.3
Isopentane	0-40	1 06 ± 0.08	0.31	0 94	40	37.2 to 47 9

*Only 21 pairs >1 ppm.
**Only 15 pairs >1 ppm

the temperatures at sampling sites were judged to range from 5 °C below to 10 °C above 25 °C.

4. Overloading of tubes and monitors could cause errors. Charcoal tubes sampled from 90 to 190 liters of air, averaging 130 liters, at 1 L/min. Only two charcoal tubes showed concentrations over 100 ppm total organic vapors assayed (120 ppm and 150 ppm). These two tubes indicated 28 and 45 ppm total vapor respectively in their back charcoal sections. For other tubes, the total collected in the back section was less than 25 percent of that in the front section. Each monitor was exposed as long as both tubes in a set. Any significant overloading of monitors would result in regression line slopes substantially below 1.0. This did not occur.
5. The back section of a tube was analyzed whenever the chromatogram of the front section showed rather high peaks. In essence, the backs were analyzed if total organic vapors assayed exceeded about 50 ppm, which occurred in roughly half the samples. It is possible that a portion of vapors collected in the tubes was missed in analyzing samples from areas with low vapor concentrations. This would tend to increase regression line slopes slightly and give substantially positive Y intercepts. The latter did not occur.
6. Tubes were analyzed 12 weeks after sampling, and monitors 17 weeks. All were kept at -7 °C in the interim. This delay may have resulted in loss of collected vapors. One could speculate that migration of vapors to the back sections of charcoal tubes during storage might account for some loss in tubes whose back sections were not assayed. Losses in the monitors might be less as the vapors would have no alternate sink. Such migration would tend to increase regression line slopes slightly.

It is the judgment of the authors that the potential errors did not significantly affect the results.

significance of findings

Since observed concentrations of substances were generally far below TLVs and permissible exposure limits (PELs), no

conclusions can be drawn from these data regarding correlation of monitors and tubes at concentrations approaching TLVs, without assuming linearity beyond the observed data.

However, since one of the anticipated values of the passive monitor is in routine monitoring, it is important to demonstrate that they can reliably measure low exposures as well as high ones. The results of this study indicate that the passive monitor reliably assayed low concentrations of mixed vapors of 20 of the chemicals mentioned equally as well as charcoal tubes, under the conditions encountered. Charcoal tube and passive monitor results differed significantly for methylcyclohexane and n-octane.

The tendency toward negative Y-intercepts (Table II) may indicate a sub-ppm detection threshold in the monitors for some chemicals. More such comparative studies are needed to build a body of literature on which to establish the applications and limitations of the passive monitor.

research support

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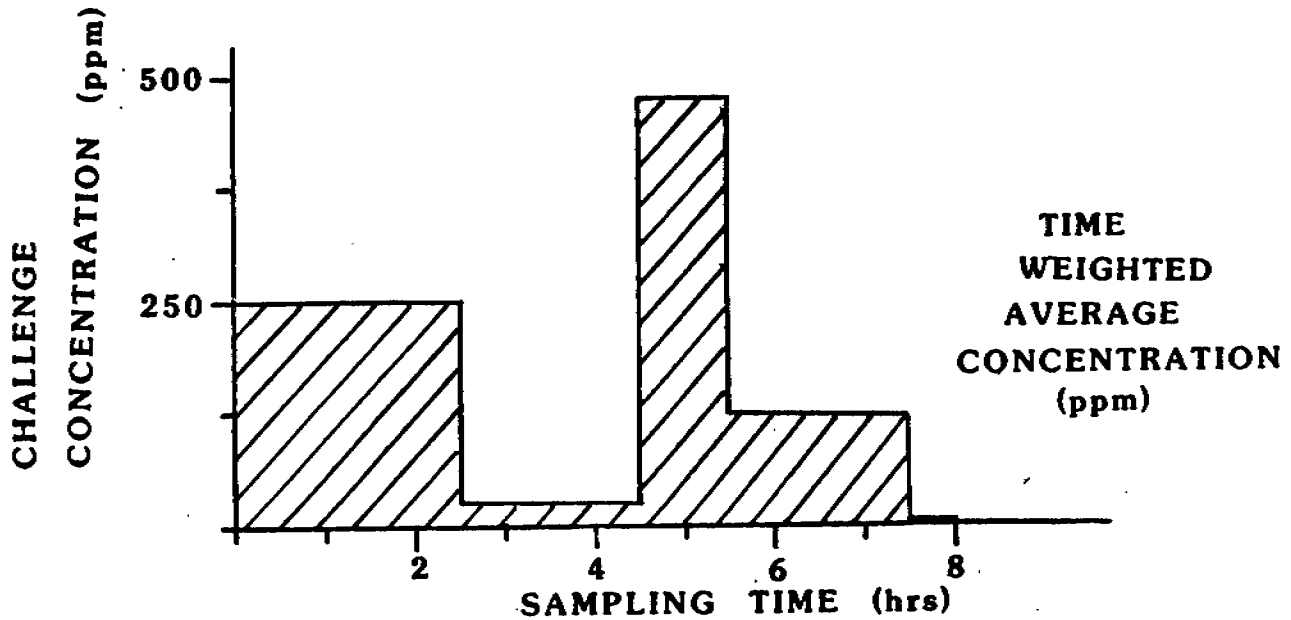
SAMPLING

VARIABLE CONCENTRATION

3M 110895

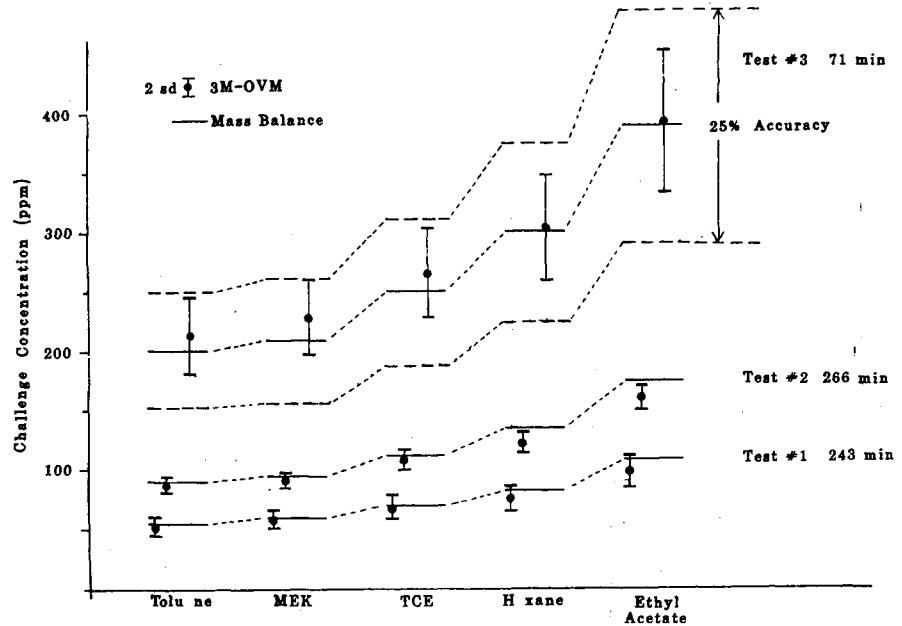
TOLUENE
VARIABLE CONCENTRATION
RH-80%



3M-OVM	246	20	479	108	180±5
Mass Balance	243	19	477	108	178
3M-OVM	—	—	—	—	196±7
Charcoal Tube	—	—	—	—	195±8
Mass Balance	—	—	—	—	179

3M 110896

SAMPLING A MIXTURE
AT VARIOUS CHALLENGE CONCENTRATION



SAMPLING

HIGH VAPOR PRESSURE

COMPOUNDS

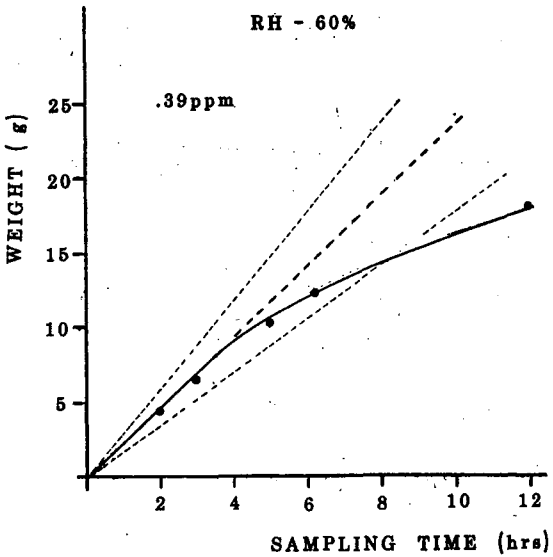
3M 110898

High Vapor Compounds

	Compound	Vapor Pressure (mm)	Boiling Point (C)	PEL (ppm)
*	Vinyl Chloride		-14	1
	Butadiene	910	4	1000
	Ethyl Ehter	442	35	400
*	Pentane	426	36	1000
	Ethyl Bromide	375	40	200
*	Dichloromethane	350	40	500
	Allyl Chloride	295	44	1
*	Acetone	226	56	1000
*	Trans 1,2 Dichloroethylene	265	48	50
	1,1 Dichloroethane	182	57	100
*	Cis 1,2 Dichloroethylene	180	60	50
*	Methyl Acetate	173	58	200
*	Chloroform	160	61	50
*	Hexane	124	69	500
	Isopropyl Ether	119	69	500
*	Bromochloromehtane	117	68	200
*	Methyl hloroform	100	74	350

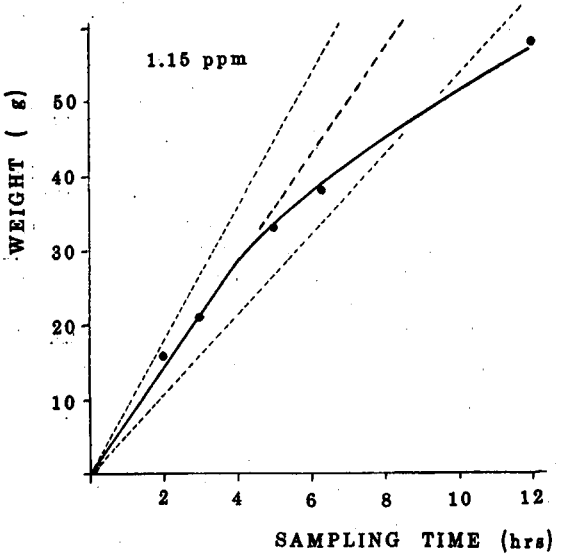
*Compounds sampled from various concentration to validate sampling rate and capacity values.

VINYL CHLORIDE



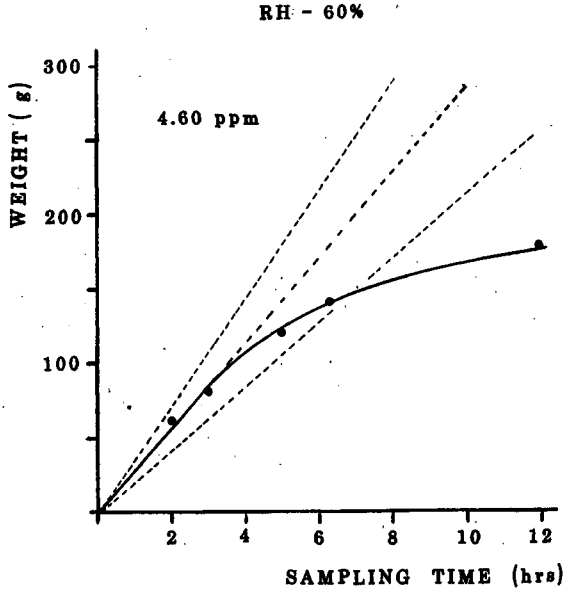
VINYL CHLORIDE

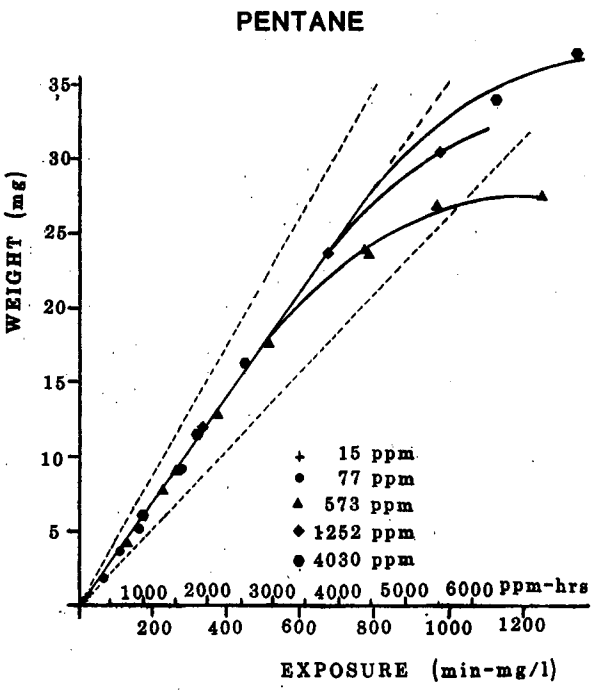
RH - 60%



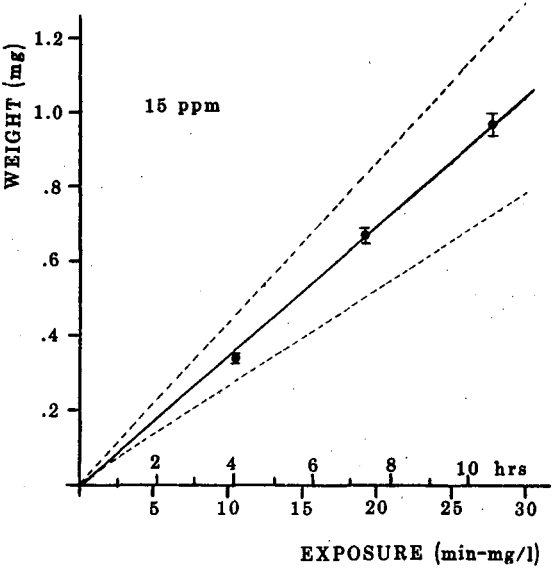
3M 110902

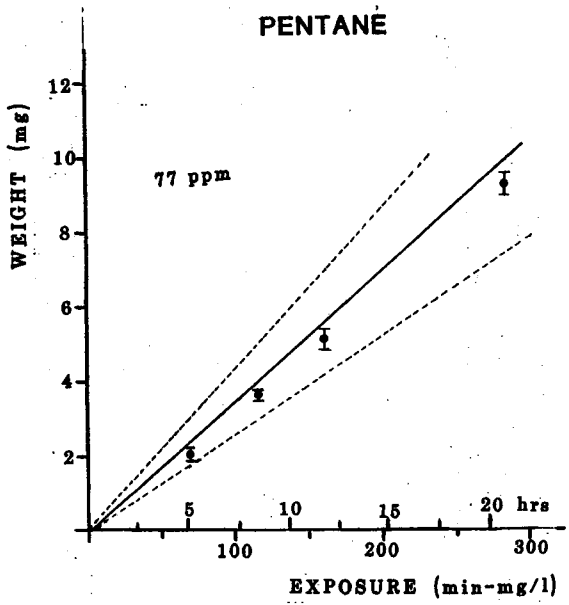
VINYL CHLORIDE




PENTANE
WEIGHT (mg)
35
30
25
20
15
10
5
15 ppm
77 ppm
573 ppm
1252 ppm
4030 ppm
1000 2000 3000 4000 5000 6000 ppm-hrs
200 400 600 800 1000 1200
EXPOSURE (min-mg/l)

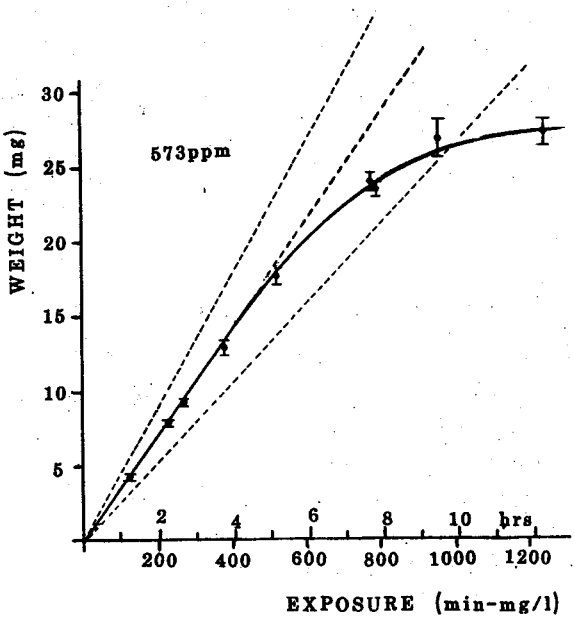
PENTANE


WEIGHT (mg)
1.2
1.0
.8
.6
.4
.2
15 ppm
2
4
6
8
10 hrs
5
10
15
20
25
30
EXPOSURE (min-mg/l)

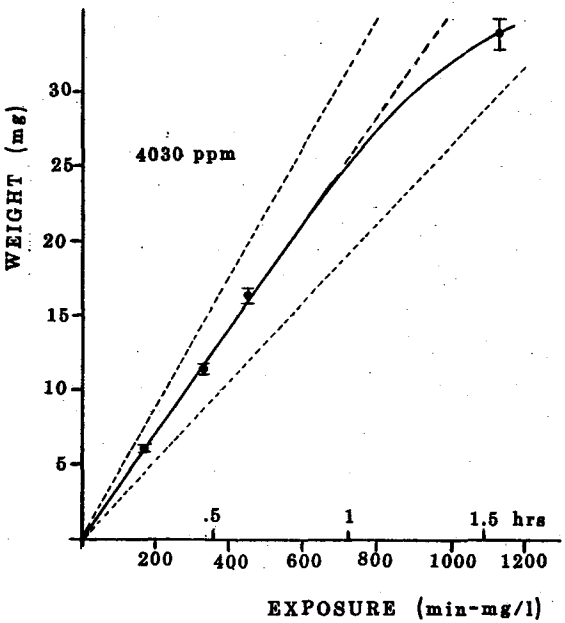

PENTANE
77 ppm
WEIGHT (mg)
12
10
8
6
4
2
5
10
15
20 hrs
100
200
300
EXPOSURE (min-mg/l)

3M 110906

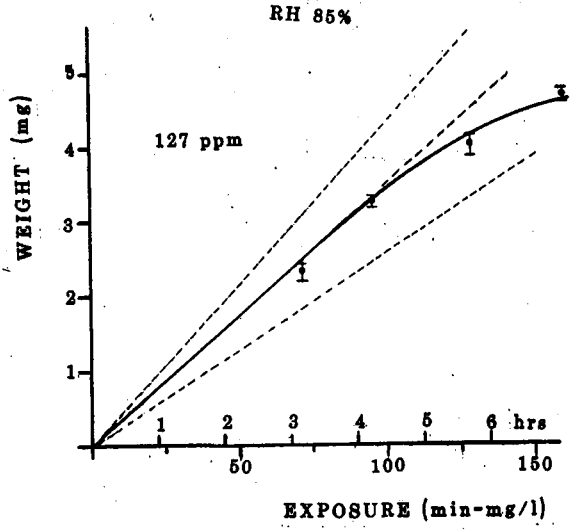
PENTANE


WEIGHT (mg)
30
25
20
15
10
5
573ppm
2
4
6
8
10
hrs
200
400
600
800
1000
1200
EXPOSURE (min-mg/l)

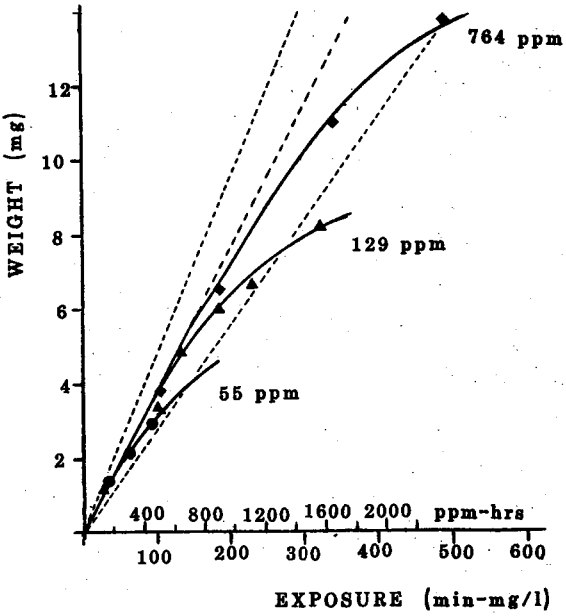
PENTANE


WEIGHT (mg)
30
25
20
15
10
5
4030 ppm
.5
1
1.5 hrs
200
400
600
800
1000
1200
EXPOSURE (min-mg/l)

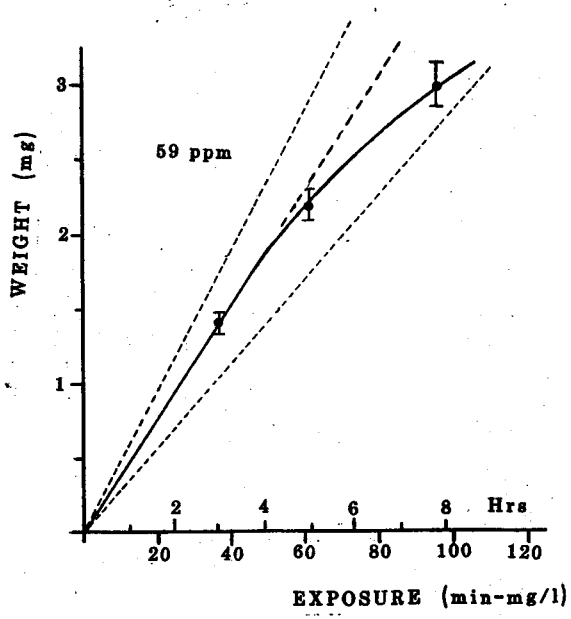
PENTANE

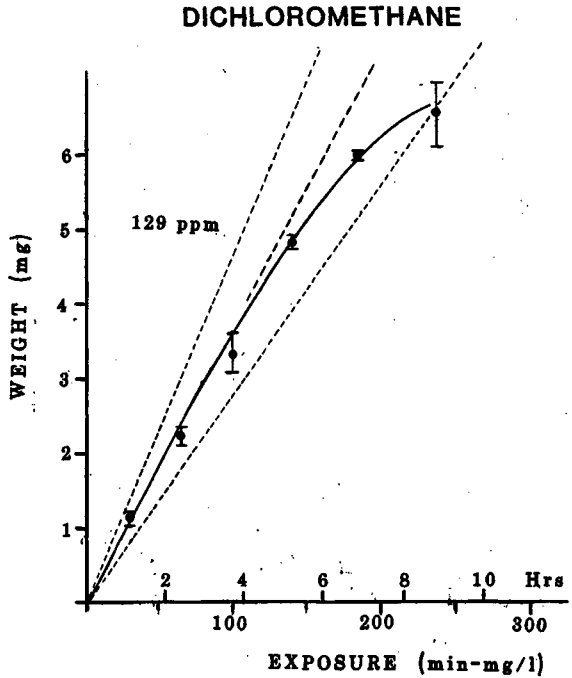

RH 85%
127 ppm
WEIGHT (mg)
1
2
3
4
5
1
2
3
4
5
6 hrs
50
100
150
EXPOSURE (min-mg/l)

DICHLOROMETHANE



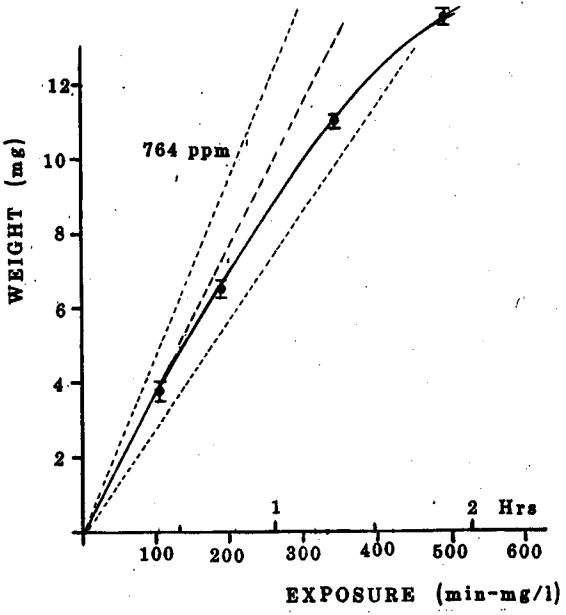
DICHLOROMETHANE

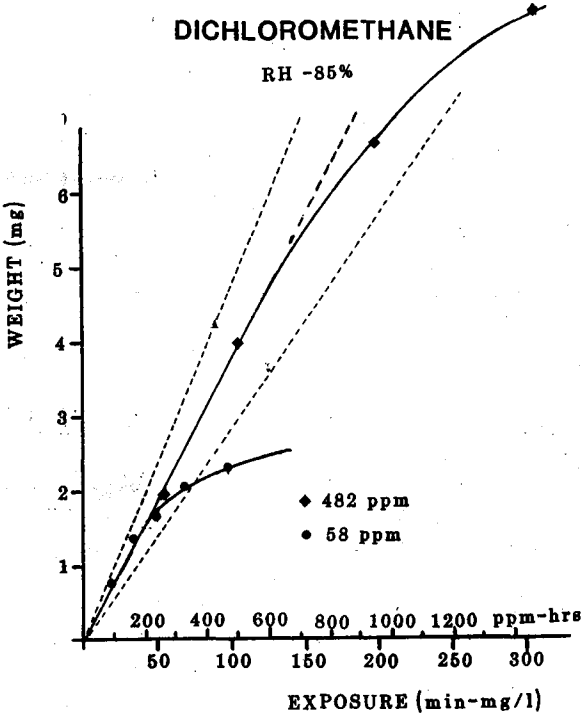



DICHLOROMETHANE
129 ppm
WEIGHT (mg)
1
2
3
4
5
6
2
4
6
8
10
Hrs
100
200
300
EXPOSURE (min-mg/l)

3M 110912

DICHLOROMETHANE

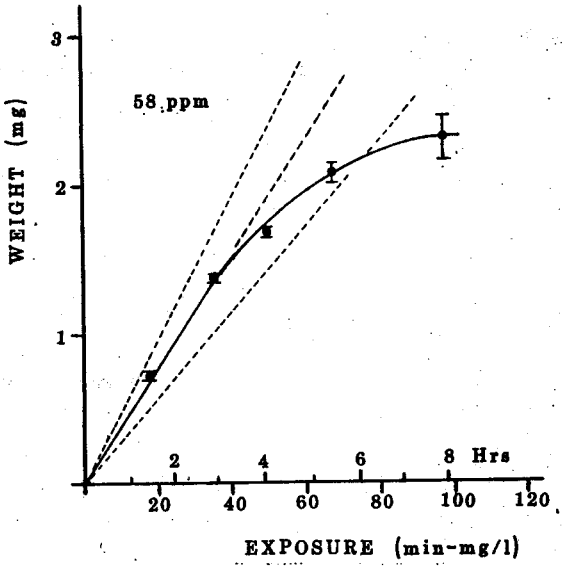



DICHLOROMETHANE
RH -85%
WEIGHT (mg)
1
2
3
4
5
6
◆ 482 ppm
● 58 ppm
200 400 600 800 1000 1200 ppm-hrs
50 100 150 200 250 300
EXPOSURE (min-mg/l)

3M 110914

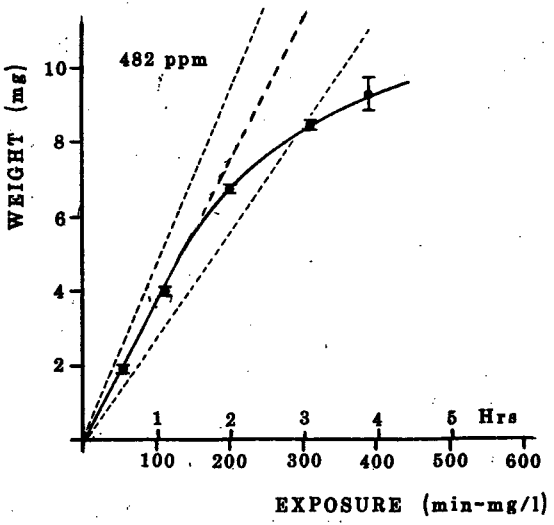
DICHLOROMETHANE

RH - 85%

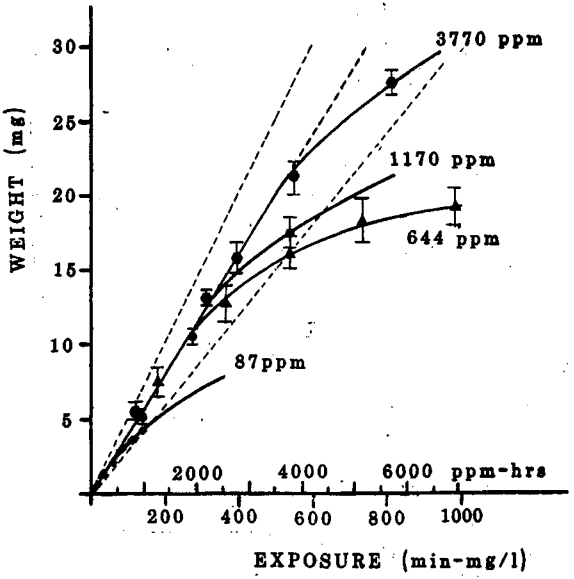


DICHLOROMETHANE

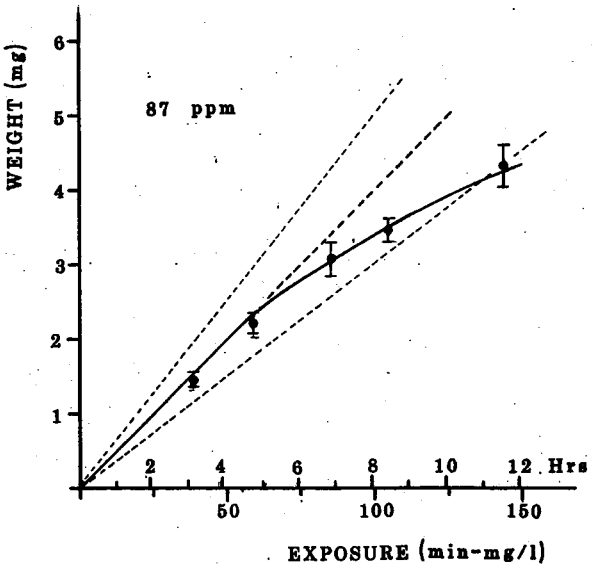
RH - 85%



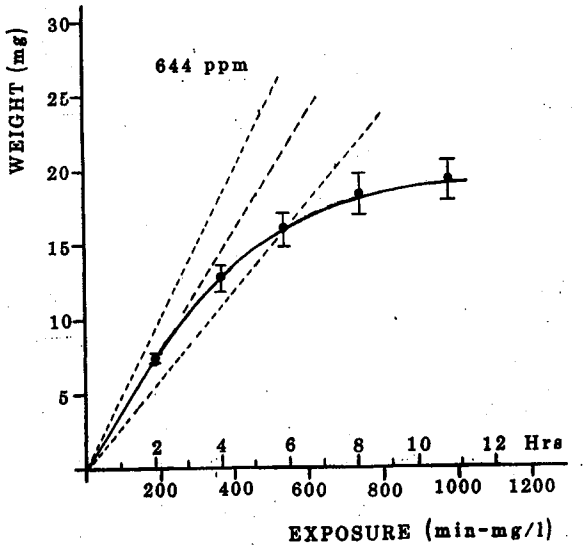
ACETONE


WEIGHT (mg)
30
25
20
15
10
5
3770 ppm
1170 ppm
644 ppm
87ppm
2000
4000
6000
ppm-hrs
200
400
600
800
1000
EXPOSURE (min-mg/l)

ACETONE

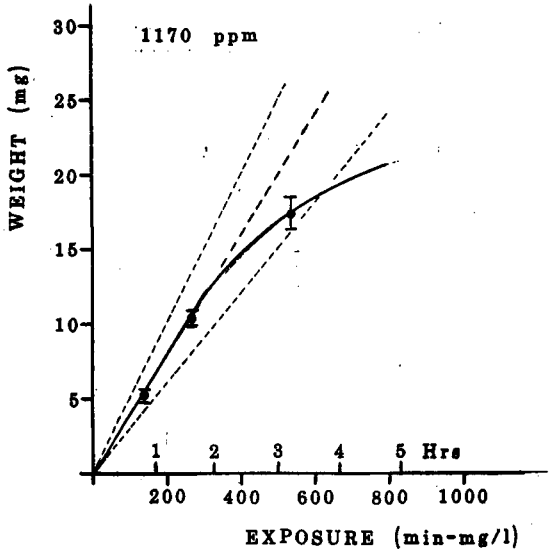

WEIGHT (mg)
87 ppm
1
2
3
4
5
6
2
4
6
8
10
12 Hrs
50
100
150
EXPOSURE (min-mg/l)

ACETONE

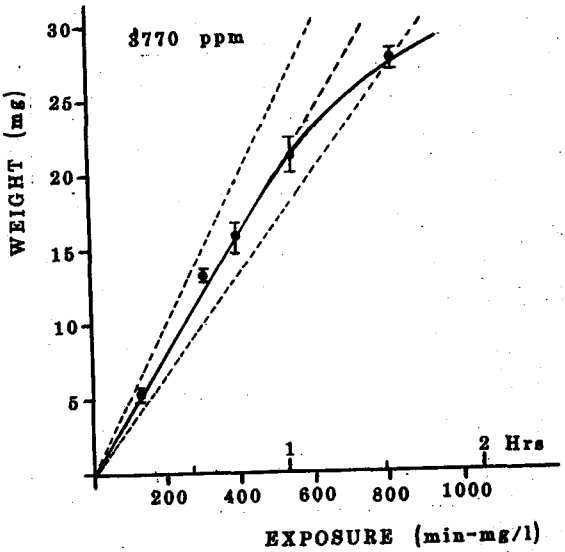


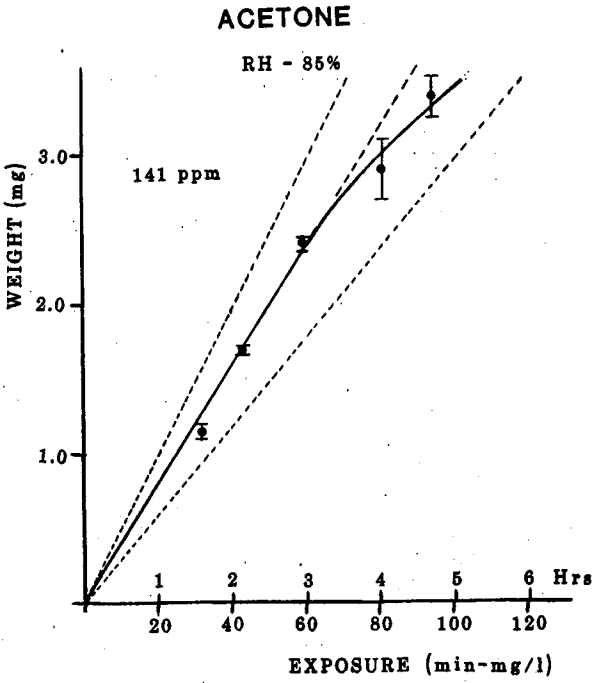
3M 110919

ACETONE


1170 ppm
WEIGHT (mg)
30
25
20
15
10
5
1
2
3
4
5 Hrs
200
400
600
800
1000
EXPOSURE (min-mg/l)

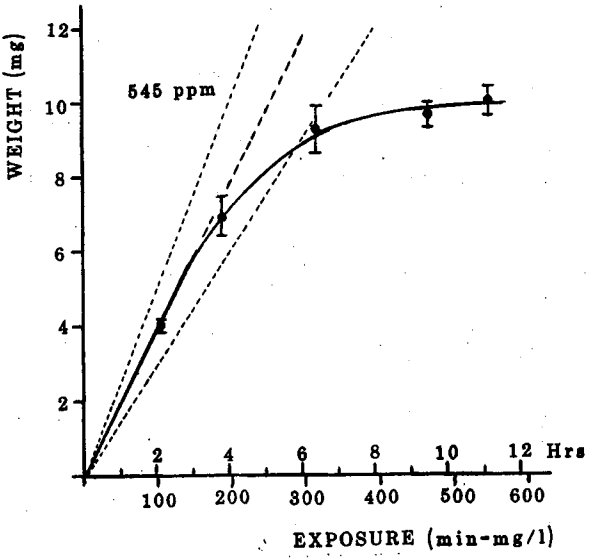
ACETONE


3770 ppm
WEIGHT (mg)
30
25
20
15
10
5
1
2 Hrs
200
400
600
800
1000
EXPOSURE (min-mg/l)

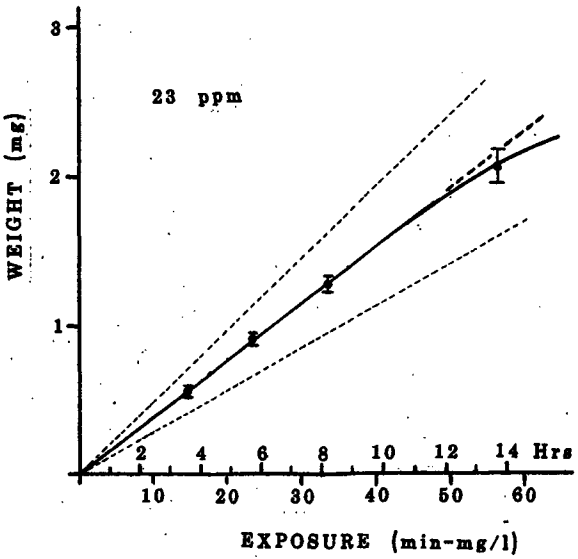

ACETONE
RH - 85%
141 ppm
WEIGHT (mg)
3.0
2.0
1.0
1
2
3
4
5
6 Hrs
20
40
60
80
100
120
EXPOSURE (min-mg/l)

ACETONE

RH - 85%

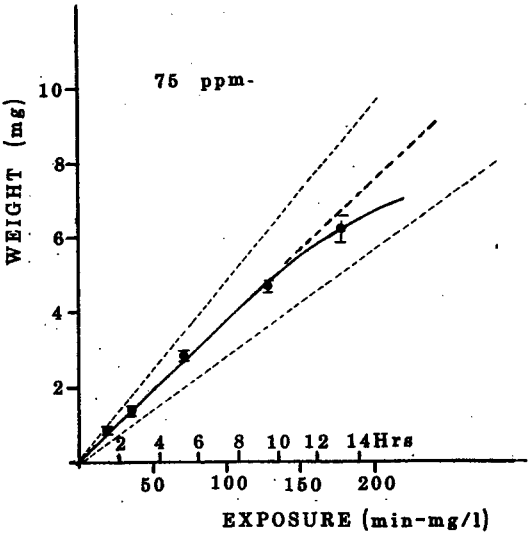


METHYL ACETATE

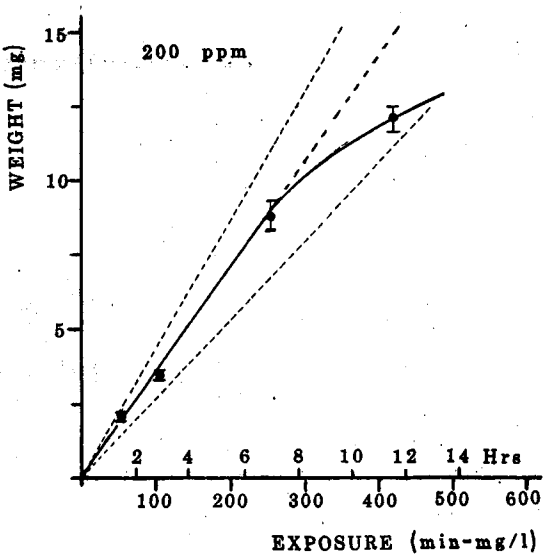


3M 110924

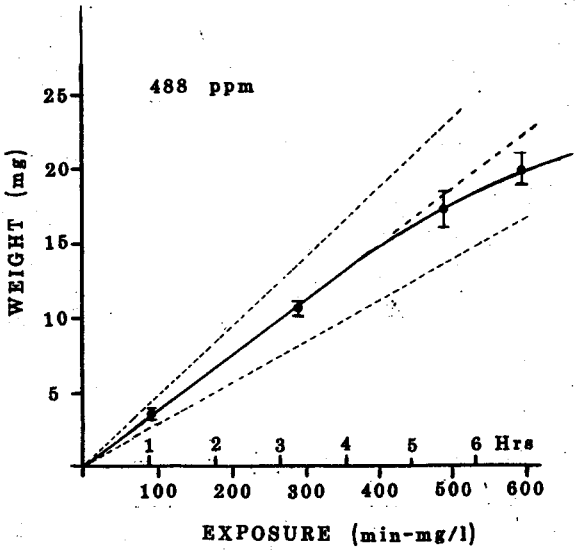
METHYL ACETATE



METHYL ACETATE

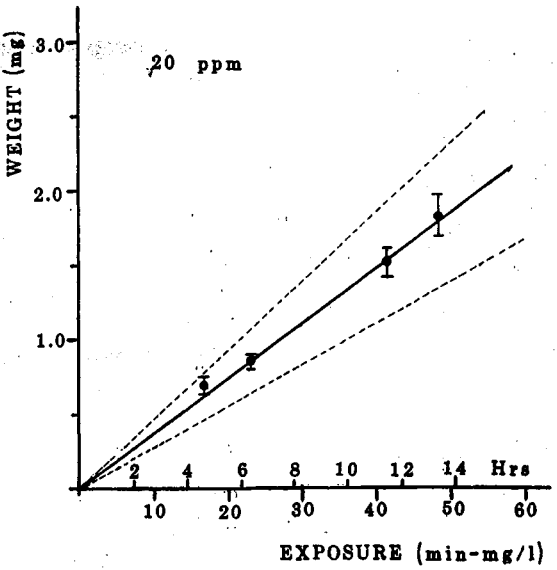


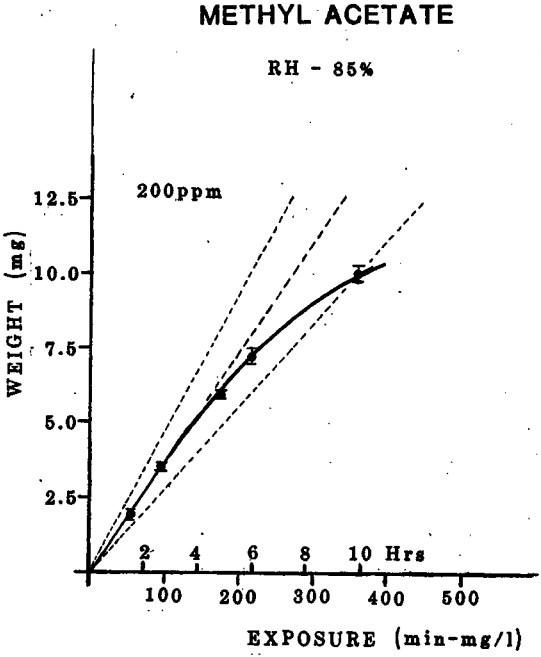
METHYL ACETATE



METHYL ACETATE

RH - 85%




METHYL ACETATE
RH - 85%
200ppm
12.5
10.0
7.5
5.0
2.5
WEIGHT (mg)
2
4
6
8
10 Hrs
100
200
300
400
500
EXPOSURE (min-mg/l)

SEI Update

December 1994 Volume 9 Issue 4

SEI UPDATE is the official newsletter of the Safety Equipment Institute. Permission to reprint is granted, with attribution to SEI appreciated.

SEI Receives OSHA Support for Dosimeter Program

The SEI Board of Directors, at their December 2, 1994 meeting, approved the initiation of a new program to certify direct reading passive monitors. This program is a natural addition to the highly successful program for certifying gas detector tube units.

SEI will use an OSHA approved **Protocol for the Evaluation of Direct Reading Passive Monitors.** Clayton Environmental Consultants will add this verification testing to their current testing of gas detector tube units. Bill Golomski will conduct quality assurance audits at participating manufacturers' facilities.

> *the success in your program to certify gas detector tubes is particularily noteworthy*

SEI will use the OSHA approved "Protocol" on an interim basis until the industry develops a consensus standard through the American National Standards Institute (ANSI). The Industrial Safety Equipment Association (ISEA) is now forming a group to begin work on a standard for passive monitoring devices. Their next meeting is January 26-27 at the OSHA Salt Lake Technical Center.

In a letter to Patricia A. Gleason, SEI President, officials from OSHA indicate they are pleased that SEI will provide third-party certification of passive monitoring devices, and state, "We also recognize the confidence manufacturers and government agencies, including NIOSH and MSHA, have demonstrated in SEI's ability to provide this service through their participation and comments regarding your existing programs. The success in your program to certify gas detector tubes is particularily noteworthy because it can be extended to cover what is needed for the certification of passive monitoring devices". This program will allow OSHA to include the device as an option for use by OSHA compliance officers. SEI expects OSHA to announce a similar recognition of SEI certified gas detector tubes.

U.S. DEPARTMENT OF LABOR
OCCUPATIONAL SAFETY & HEALTH ADMINISTRATION
Salt Lake Technical Center
1781 South 300 West P.O. Box 65200
Salt Lake City, UT 84165-0200

December 16, 1994

Patricia A Gleason, President
Safety Equipment Institute
1901 North Moore Street, Suite 808
Arlington, VA 22209

Dear Ms. Gleason:

Thank you for the opportunity to review the protocol you are considering for evaluating direct reading passive monitors, such as the ACT™ badges manufactured by Envirometrics Products Company. We are pleased that manufacturers of passive monitoring devices are considering funding the Safety Equipment Institute(SEI) to provide "third party certification" of the effectiveness of these devices. As you know, OSHA strongly supported the need for this type of verification in its recent expansion of the personal protective equipment standard (Ref. 29CFR1910.132, April 26, 1994). We also recognize the confidence manufacturers and government agencies, including NIOSH and MSHA, have demonstrated in SEI's ability to provide this service through their participation and comments regarding your existing certification programs. The success in your program to certify detector tubes is particularly noteworthy because it can be extended to cover what is needed for the certification of passive monitoring devices.

Published field studies indicate a large variability in workplace exposures. Therefore, we want to encourage employers to obtain multiple samples for varying working conditions to obtain a more realistic characterization of workplace exposures. The availability of effective, inexpensive, and easy to use devices, such as passive monitors, provides a needed resource to employers to achieve this objective. Unfortunately, our evaluations of early passive monitors identified problems with some of the devices on the market. The existence of a certification program to verify the claims of the manufacturers will greatly assist employers in identifying those devices which will be effective in monitoring their work sites. The program should also improve the overall quality of these devices as manufacturers strive to meet a higher "industry standard".

This brings us to the issue at hand. We recognize that the development of generic protocols for evaluating passive monitoring devices is being considered by both OSHA and ANSI. However, based on current knowledge, a successful evaluation of direct reading passive monitors by your protocol (as modified) would allow us to include the device as an option for use by OSHA compliance officers. Also, recognizing our common goal of providing employers with a variety of effective tools for evaluating workplace hazards, please let us know if we can be of assistance in reviewing specific protocols for other types of sampling devices.

Sincerely yours,

Robert A. Curtis, Director
OSHA Health Response Team

Rick Cee, Chief
Field Instruments Team

Comments on Evaluation Protocol for Direct Reading Passive Monitors

Introduction

The following comments are presented based on our review of the draft protocol. These comments are presented as elements for a "third party certification" of a direct reading passive monitor and it should be understood that the manufacturer would perform a more thorough validation during development of the devices. The evaluation of passive devices should evaluate the manufacturer's claims of accuracy over the range of operating conditions for which the devices are supposed to work. These conditions normally include, but are not limited to, concentration, temperature, relative humidity, face vel city, exposure time, interferences, sample stability, analytical variability, and shelf life.

Unless otherwise stated, each exposure test will be conducted with 10 monitors for statistical analysis, and will use standard exposure conditions of 25 degrees C, 50% relative humidity, 25 cm/s face velocity, and the appropriate OSHA PEL or ACGIH TLV concentration for the analyte being tested. All tests are conducted using the manufacturer's specified operating parameters for the monitor (e.g., exposure time, shelf life, etc.). Normally, the two worst case extremes of the operating parameters and one or two intermediate values should be evaluated.

Concentration and Exposure Time

A concentration of 0.1 times the appropriate PEL or TLV may be evaluated instead of 0.25, as recommended in the draft NIOSH protocol, and the UK and European protocols. Normally, 2 times the appropriate PEL or TLV is used instead of 1.25. Testing at 0.75 times the exposure standard may be unnecessary. Expose the monitors for the specified period of time described in the manufacturer's literature.

Temperature and Relative Humidity

The two extremes and a midpoint of the ranges specified in the manufacturer's literature should be evaluated for both temperature and humidity.

Pressure

Evaluate the adequacy of the manufacturer's instructions for reporting the results of monitoring at conditions other than 760 mm atmospheric pressure.

Face Velocity

The performance of the monitor should be evaluated in the air velocity range of 10 to 150 cm/s normally found in workplaces, as recommended by NIOSH, unless otherwise specified by the manufacturer's literature.

Interferences

Assess whether the manufacturer has adequately addressed potential positive and negative interferences based on the reaction chemistry used in the monitors. Where potential negative interferences have been documented in the literature, but have not been sufficiently evaluated by the manufacturer, the user manual will instruct the user to conduct initial side-by-side sampling with alternative methods to assess the amount of interference occurring at the specific work site, or the manual will explicitly state that the monitors can not be used in this type of environment.

Where interferences have been identified by the manufacturer, expose monitors to the interferences at their PEL for the maximum sampling time period. Verify that the manufacturer has documented and evaluated the extent of known interferences.

Shelf Life

To verify shelf life, monitors will be stored per manufacturer's instructions (e.g. refrigerated if required by the user manual) and tested at standard conditions (i.e., 25 cm/s, 50% RH, PEL or TLV, and 25 Celsius) immediately prior to the expiration date if possible. Monitors may be given an initial certification based on an evaluation of manufacturer's tests of maximum shelf life.

Quality Control

Acceptable as proposed.

Monitor Orientation

Expose monitors at orientations parallel and perpendicular to air flows for each type of badge design.

Reverse Diffusion

Expose 20 monitors to a 2X exposure limit for 0.5X the maximum specified sampling time and to 0% exposure limit for 0.5X the maximum specified sampling time. Use worst case temperature and humidity conditions.

Inter-reader Variability

For direct reading dosimeters, inter-reader variability, either electronic or visual, must be assessed and incorporated into overall accuracy of the system. An example protocol for testing visual precision may be found in the SEI detector tube certification protocol.

Readout Time

Evaluate the maximum time allowed between cessation of sampling and measurement of exposure or specify that devices must be read out immediately.

Evaluation of Qualitative Monitors

A similar validation protocol to the quantitative monitors can be applied to qualitative monitors. Qualitative monitors are read visually by comparing the developed color to reference color guides provided on the card (some monitors have one reference guide). The color guides typically represent the action level and the PEL for PEL-TWA cards (8 hours). The color on the STEL or CEILING cards are based on the ACGIH STEL or OSHA CEILING standards respectively. The intensity of the developed color in relation to the color guide provides an indication of the exposure concentration.

Field Evaluation

Field evaluation of passive monitors in actual workplaces is encouraged. When possible, samples should be taken side-by-side with a reference method in industrial settings. Any shortcomings of the reference method should be taken into account when comparing the test method. The manufacturer should be encouraged to conduct the field test. The third party certifier should be capable of reviewing the manufacturer's field data for adequacy. Field testing can be conducted using criteria established in the NIOSH, Health and Safety Executive, CEN or other protocol using should scientific principles and practices.

Standards/Testing Agencies

The standards, testing agencies and auditors selected by SEI are:

PRODUCT CATEGORY	SELECTED APPLICABLE STANDARD	TESTING LABORATORY	QUALITY ASSURANCE
Disposable Coveralls	ANSI/ISEA 101-1993	Professional Service Industries, Inc. PTL Division	W.A. Golomski & Associates
Emergency Eyewash and Shower Equipment	ANSI Z358.1-1990	Professional Service Industries, Inc. PTL Division	W.A. Golomski & Associates
Eye & Face Protection	ANSI Z87.1-1989	Professional Service Industries, Inc. PTL Division	W.A. Golomski & Associates
Fire Service Life Safety Rope, Harness, and Hardware	NFPA 1983, 1995 Edition	Professional Service Industries, Inc. PTL Division	W.A. Golomski & Associates
Gas Detector Tube Units	ANSI/ISEA 102-1990	Clayton Environmental Consultants, Inc.	W.A. Golomski & Associates
Gloves for Structural Fire Fighting	NFPA 1973, 1993 Edition	ETL Testing Laboratories, Inc.	Quality Improvement Corporation
Headgear Used in Horse Sports and Horseback Riding	ASTM F-1163-95	ETL Testing Laboratories, Inc.	W.A. Golomski & Associates
Helemts for Structural Fire Fighting	NFPA 1972, 1972 Edition	ETL Testing Laboratories, Inc.	W.A. Golomski & Associates
Liquid Splash-Protective Suits for Hazardous Chemical Emergencies	NFPA 1992, 1994 Edition	ETL Testing Laboratories, Inc.	W.A. Golomski & Associates

Open-Circuit Self-Contained Breathing Appartus for Fire Fighters (SCBA)	NFPA 1981, 1992 Edition	ETL Testing Laboratories, Inc.	Quality Improvement Corporation
Passive Dosimeters	Protocol for Evaluation of Direct Reading Passive Monitors	Clayton Environmental Consultants	W.A. Golomski & Associates
Personal Alert Safety Systems (PASS) for Fire Fighters	NFPA 1982, 1993 Edition	ETL Testing Laboratories, Inc.	Quality Improvement Corporation
Prescription Safety Eyewear	ANSI Z87.1-1989	Professional Services Industries, Inc. PTL Division	W.A. Golomski & Associates
Protective Clothing For Emergency Medical Operations	NFPA 1999, 1992 Edition	ETL Testing Laboratories, Inc.	W.A. Golomski & Associates
Protective Gloves For Emergency Medical Operations	NFPA 1999, 1992 Edition	ETL Testing Laboratories, Inc.	Quality Improvement Corporation
Protective Clothing for Proximity Fire Fighting	NFPA 1976, 1992 Edition	ETL Testing Laboratories, Inc.	W.A. Golomski & Associates
Protective Clothing for Structural Fire Fighting	NFPA 1971, 1991 Edition	ETL Testing Laboratories, Inc.	W.A. Golomski & Associates
Protective Clothing and Equipment for Wildland Fire Fighting (Helmets)	NFPA 1977, 1993 Edition	ETL Testing Laboratories, Inc.	W.A. Golomski & Associates
Protective Clothing and Equipment for Wildland Fire Fighting (Clothing)	NFPA 1977, 1993 Edition	ETL Testing Laboratories, Inc.	W.A. Golomski & Associates
Protective Clothing and Equipment for Wildland Fire Fighting (Footwear)	NFPA 1977, 1993 Edition	ARTECH Corporation	Quality Improvement Corporation
Protective Footwear for Structural Fire Fighting	NFPA 1974, 1992 Edition	ARTECH Corporation	Quality Improvement Corporation
Protective Headgear Used in Bicycling	ASTM F 1447 - 94	ARTECH Corporation	Quality Improvement Corporation
Protective Headwear for Industrial Workers	ANSI Z89.1-1986	ETL Testing Laboratories, Inc.	W.A. Golomski & Associates
Station\Work Uniforms for Fire Fighters	NFPA 1975, 1994 Edition	ETL Testing Laboratories, Inc.	W.A. Golomski & Associates

3M 110936

Support Function Protective Garments For Hazardous Chemical Operations	**NFPA 1993, 1994 Edition**	**ETL Testing Laboratories, Inc.**	**W.A. Golomski & Associates**
Vapor-Protective Suits for Hazardous Chemical Emergencies	**NFPA 1991, 1994 Edition**	**ETL Testing Laboratories, Inc.**	**W.A. Golomski & Associates**

If you require additional information or have questions about the SEI third-party certification programs for safety equipment, please do not hesitate to *contact our Office* **703/525-3354.**

Introduction **Board and Staff** **Certified Product List** **Suppliers**

Standards/Testing Agencies **What's New** **Information Request Form** **Contact/Staff Information**

SEI Home

sei_headquarters@msn.com

3M 110937

SENSIDYNE

MEMORANDUM

TO: Distribution

FROM: Ron Roberson

DATE: August 1, 1995

SUBJ.: **SEI Badge Certification**

Attached is some correspondence between Sensidyne and SEI concerning SEI's closed certification of Envirometrics Company's formaldehyde badge. I feel that SEI acted unfairly by not opening the certification opportunity to other companies. I have asked Sensidyne and Gastec not to participate in SEI's badge certification program, but to conduct our own program verifying with lab reports that the product meets the ANSI requirements. I have also asked Sensidyne and Gastec to carefully evaluate any benefit we receive from our current SEI certifications on our short term detector tubes.

If you have questions or comments, please contact the writer at 1(800)451-9444.

Sincerely yours,

Ron Roberson

Ron Roberson
Corporate Industrial Hygienist

Copy: Kim Chapman, Gilian Environmental
Gus Manning, Assay Technology
Alan Levin, Air Scan
Richard Wanek, GMD/Bacharach
Bob Weber, 3M
Ed Ligus, National Draeger
Katie Spear, MSA
Lloyd Kent, Matheson Gas

SENSIDYNE

SENSIDYNE INC.
Gas and Particulate Detection Systems
16333 Bay Vista Drive, Clearwater, Florida 34620
800-451-9444 / Florida 813-530-3602
TELEX 756223 / Fax 813-539-0550

June 1, 1995

Safety Equipment Institute
1901 North Moore Street
Arlington, VA 22209
Attn: Patricia Gleason

Dear Ms. Gleason:

As you are aware Sensidyne and Gastec have participated in SEI's detector tube certification program since it's inception. Since the beginning of our relationship with SEI, I have consistently been impressed with the degree of professionalism within SEI. SEI has historically operated in an unbiased fashion in dealing with both ISEA members and non-members in the same program. Until recently I had never witnessed favoritism toward any singl company.

SEI's detector tube certification program began with SEI contacting all th manufacturer's to solicit interest. Following that a protocol was adopted, gases selected and a test schedule published. Every company that produced detector tubes for the U.S. market was given an equal opportunity to participate. No single company was given any chance to obtain an unfair market advantage under SEI's program. To this day that professional, non-biased practice is still demonstrated in SEI's detector tube program.

Recently at the AIHC in Kansas City, Envirometrics Products Company was advertising an SEI-approved formaldehyde badge. I thought this to be false advertising since SEI's program was not yet started. However, upon checking at the SEI booth I was informed that Envirometrics had received certification in a special testing session they had requested. I was given a copy of SEI's May, 1995 newsletter that announced Envirometric's certification. I received my copy in the mail after my return from the AIHC.

I have followed SEI's commitment to a badge program carefully. Sensidyne sent representatives to the ISEA badge meetings at the National Safety Congress in October, 1994 and Salt Lake City in January, 1995. I sent correspondence to SEI with questions following the December 1994 newsletter announcement of SEI's intention to start the program. Judith Bailey answered these questions with a letter dated 12/1/94. There should have been no question that Sensidyne and Gastec were interested in this program, yet we were not informed that testing had started. Bill Emy of ISEA estimated two years from January, 1995 for ISEA to complete the ISEA test protocol. We were not informed by SEI that SEI planned to start without that protocol.

SENSIDYNE

SENSIDYNE INC.
Gas and Particulate Detection Systems
16333 Bay Vista Drive, Clearwater, Florida 34620
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It is apparent that Envirometrics quietly pushed for a custom certification in order to obtain a market advantage on the other badge manufacturers. I am very disappointed that SEI supported this market advantage. It is clearly not within SEI's historical policy to provide a custom certification that was apparently not open to everyone. It is clearly not the actions of a responsible unbiased third party certifier to support one manufacturer at the expense of others.

Please answer the following questions in writing so I can advise Sensidyne and Gastec on future dealings with SEI.

1) When did the passive monitor program begin? Was a test schedule announced? Why was Sensidyne not informed prior to testing? We advertise formaldehyde passive monitors.

2) Why was Envirometrics allowed to certify a product without soliciting other program participants? Is it SEI's policy to conduct custom certifications outside of published programs?

3) The following companies also advertise passive formaldehyde monitors. Which ones were informed of SEI's formaldehyde certification testing?

   a) Gilian Environmental
   b) Assay Technology
   c) Air Scan
   d) GMD
   e) 3M

4) Why did SEI not follow the procedure set forth by the detector tube program? Why were the following steps omitted?

   a) Soliciting interested companies
   b) Publishing a test gas list
   c) Publishing a test schedule
   d) Informing manufacturers of certification opportunity

5) Why did SEI rush a custom certification for a single manufacturer? Did SEI intend to provide one company with a marketing advantage? Did SEI not realize the rush to certify in time for a major trade show promotion?

SENSIDYNE

SENSIDYNE INC.
Gas and Particulate Detection Systems
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TELEX 756223 / Fax 813-539-0550

I believe that SEI did not act responsibly in this initiation of a new program. I believe that all manufacturers should be given an equal opportunity to submit products if an unbiased third party certification truly exists. In my opinion SEI should do the following to rectify the situation.

1) Contact all companies that produce passive monitors and ask if they wish to participate in a certification program for formaldehyde monitors. Provide the test protocol to interested parties.

2) Produce a test schedule allowing all interested parties adequate time to submit products.

3) Inform all the manufacturers of the program schedule.

4) Put Envirometric's certification on "hold" to be released with the other participant's certifications.

Please respond in writing as to SEI's planned actions to rectify this situation. Our continued support of SEI is pending SEI's response.

Sincerely,

Ron Roberson
Corporate Industrial Hygienist

RR/tr

copy:Gilian Environmental
Assay Technology
Air Scan
GMD
3M

SEI Certifies 1st Passive Monitor

The first certification for direct reading passive dosimeters was issued to the Envirometrics Products Company for their ACT Monitoring Card System For Formaldehyde. Verification testing was conducted by SEI contract lab, Clayton Environmental Consultants, Inc. Envirometrics passed the SEI quality assurance audit which was conducted by William A. Golomski & Associates.

A protocol, which underwent a thorough review by OSHA's technical staff in Salt Lake City, is being used as the basis for the new program. SEI plans to use this interim standard until a consensus standard is published by ANSI. The Industrial Safety Equipment Association has formed a standards group to accomplish this task.

Equestrian Safety

(Continued from page 3)

Task Group Chair, Dru Malavase's suggestion, SEI is cosponsoring a poster that will reach thousands of equestrian riders. Among others, another sponsor of the poster is the American Medical Equestrian Association. The poster includes a photo of Christopher Reeve riding his horse, Denver, and includes a quote, *"In films I've played an invincible hero - but in real life, I wouldn't think of riding without a helmet."* The poster will be distributed nationwide.

OSHA Recognizes SEI Certification

OSHA maintains a Chemical Information File containing substances encountered by compliance officers in their workplace audits. SEI certified Gas Detector Tubes and Passive Monitors will now be listed in this File as a recommended screening device for OSHA compliance officers. This database is available to the public through the GPO and accessible via the Internet. This recognition by OSHA is a tremendous boost for companies with certified products to gain national exposure.

SEI Update

SAFETY EQUIPMENT INSTITUTE
1901 N. Moore Street
Arlington, VA 22209
Tel: 703/525-3354
Fax: 703/528-2148

SEI's May 1995 Newsletter

inside...

SEI - Your Symbol of Quality in Safety Equipment

SAFETY EQUIPMENT INSTITUTE
1901 North Moore Street
Arlington, VA 22209

703/525-3354
703/528-2148 Fax

June 6, 1995

Mr. Ron Roberson
Sensidyne Inc.
16333 Bay Vista Drive
Clearwater, FL 34620

Dear Ron:

In response to your June 1, 1995 letter I would like to address your statements about SEI's continued professionalism in operating certification programs for safety and protective equipment. SEI's purpose continues to be to assist government agencies along with users and manufacturers of safety and protective equipment in meeting their mutual goals of protecting those who use safety and protective equipment on or of the job, in keeping with recognized standards and the current state of the art, and to recognize, for the convenience of users, those products which are certified to meet applicable standards.

In all programs we attempt to provide a fair and equal opportunity to companies interested in participating in SEI certification programs. SEI is a non-profit organization with no interest in providing any company a market advantage. SEI's sole purpose is to test and certify products and to fill a void in the industry because of the lack of a government certification program for safety and protective equipment. We are proud of our accomplishments over the years and the tremendous growth and recognition of SEI's certification programs in general industry, the fire service and by consumers.

In May of 1994 we had our first discussion with OSHA personnel about their interest in recognizing SEI certified gas detector tubes and passive monitors. The OSHA staff was already in the process of a review of a modification of the NIOSH protocol for passive monitors, which we thought could be used as the basis for an SEI certification program until a standard was published through ANSI. We were pleased at OSHA's interest and first publicized this exciting news on the cover of the August 1994 edition of SEI's participant newsletter, *SEI Update*.

To provide momentum to maintain OSHA's interest in recognizing SEI certified tubes and passive monitors, we decided to inform all SEI gas detector tube participants at a special meeting during the National Safety Congress on October, 25, 1994. With OSHA's level of interest being so strong, we invited two of the top OSHA Salt Lake City officials

to tell SEI participants first hand about their impending recognition of SEI certified products. At that meeting, a draft Interim Protocol for Direct Reading Passive Monitors was distributed to all attendees. Again it was emphasized that such a protocol would be reviewed by OSHA and be utilized by SEI until an ANSI standard was published. With the length of time it takes to develop a standard, utilizing an interim standard would address the short term need to support OSHA. The primary reason for holding the October 25 meeting was to announce the new SEI program, obtain input on the draft protocol and to gauge the level of interest of SEI participants. From our discussions and observations at the meeting, the first company that expressed interest in an immediate certification to the Interim Protocol was Environmetrics, Inc.

A preliminary, open meeting was held the same day by the Industrial Safety Equipment Association (ISEA) to discuss the development of an ANSI standard. Those companies ISEA thought to be manufacturers of passive dosimeters were invited to attend the ISEA meeting. OSHA representatives attended that meeting as well to discuss their interests in development of a standard. We made certain all SEI participants were included in the invitation list. While the focus of the meeting was on development of an ISEA/ANSI standard for passive monitors, the new SEI program was discussed and the draft Interim Protocol was distributed. I understand their were five companies that attended that meeting and that Mike Marselli represented Sensidyne.

Following the October meeting, Tom Augherton received a letter from you inquiring about several issues, including audit costs for the passive monitor program. Judith Bailey responded with information available at the time.

Over the next few months, OSHA continued their review of the Interim Protocol with SEI's insistence that it be generic so that it could be used for certifying similar passive monitors made by competing manufacturers. Input was also obtained from SEI's testing laboratory, Clayton Environmental Consultants and from a representative of 3M who was unable to attend the October meeting. This information was circulated to OSHA for review with the interim Protocol which received a final review from Robert Curtis and Rick Cee.

On December 2, 1995 the above information was presented to the SEI Board of Directors, who at that time approved the initiation of a program to certify passive monitors to the interim Protocol for the Evaluation of Direct Reading Passive Monitors. The intent is to utilize this standard until an ANSI standard is published. SEI announced this news on the front cover of the December 1995 issue of *SEI Update*.

At this time SEI requested a fee schedule from Clayton and some time later we were notified by telephone that the fee structure was the same as the gas detector tube program.

A subsequent ISEA meeting was held at the OSHA Salt Lake Technical Center on January 26-27, 1995 to finalize a strategy for developing a consensus standard through ANSI. At that meeting, the final OSHA reviewed interim protocol was distributed and attendees were informed of SEI initiating its certification program. Bob Curtis of OSHA notified attendees of their intent to recognize SEI certified passive monitors after March 1, 1995. That meeting was well attended with eleven manufacturers present and Clayton Environmental Consultants was available for any questions about the SEI certification program. We received no indicator of interest from any manufacturer, except Environmetrics Inc. following any of these meetings. When Environmetrics applied for SEI certification, we initiated a certification process for their formaldehyde monitor. Publishing a test schedule for one company and one monitor seemed unnecessary.

We sincerely believe there was a miscommunication with Sensidyne. Because of the unresolved cost issues surrounding your continued participation in the gas detector tube and our apparent misunderstanding of your company's dissatisfaction with fee structure, outlined in your February 3, 1995 letter, we assumed that Sensidyne was not interested in pursuing another round of testing. We would have been pleased to include any interested company in the initial certification. I am certain that Environmetrics would have appreciated the cost reduction in testing fees. SEI's role in certifying the formaldehyde monitor assisted OSHA who was looking for products independently certified by a third party. With this program, SEI was trying to meet the needs of a government agency, and not any one manufacturer.

We are making real progress in improving the management of the gas detector tube program. As always, we would like to accommodate any certification needs that you may have. If there are any passive monitors that you wish to have certified using the interim Protocol, please advise Tom Augherton, Judith Bailey or me. We can solicit other manufacturers to determine if they would like to participate.

In virtually all of SEI's other certification programs, participants submit products for certification at varying times. The unique nature of the gas detector tube program and passive dosimeter program allow for cost reductions through joint testing. Ron, we apologize for the miscommunication, and will make every effort to take that extra step in contacting all companies for future testing, even if there is no perceived interest.

Sincerely,

Patricia A. Gleason
President

SENSIDYNE

SENSIDYNE INC.
Gas and Particulate Detection Systems

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800-451-9444 / Florida 813-530-3602
TELEX 756223 / FAX 813-539-0550

June 20, 1995

Safety Equipment Institute
1901 North Moore Street
Arlington, VA 22209

Attn: Patricia Gleason

Dear Ms. Gleason:

Thank you for your letter of 6/6/95 responding to my letter of 6/1/95. I have spent the last ten years developing a very good rapport with SEI, and my recent letters of complaint were difficult ones for me to write. I believe your conclusion of miscommunication is a valid one regarding the issue of the seemingly closed passive badge certification for Envirometrics. However, my opinion that SEI acted unfairly is not changed, and I still believe that SEI should start the certification program over using SEI's protocol developed in the detector tube program.

SEI's announcement of the intended badge certification program as stated in the December 1994 newsletter is just that. It is an announcement that SEI intends to eventually have a program. There is no start date, no list of intended gases and no invitation for manufacturers to contact SEI for such information. It is simply an announcement that OSHA is interested. I received similar information from Tom Augherton in telephone conversations over the past two years. I was fully aware that SEI intended to certify badges in the future. I was never informed as to when testing would begin. Evidently no other company except Envirometrics was informed either.

My company attended the two meetings referenced in your letter. No start date was given at either meeting. The 10/25/95 meeting was simply to solicit interest from manufacturers. SEI gave no indication that the testing was actually about to start. The Salt Lake City meeting of 1/26 and 1/27/95 was to initiate the writing of the ISEA/ANSI standard. There was no announcement that SEI would start a program prior to that standard's completion.

I attended the Salt Lake City meeting personally and there were no SEI personnel present. Bill Emy of ISEA announced that Marshall Parker of Clayton would represent SEI at that meeting. Mr. Parker stated that their lab fees would be similar to the detector tube lab

fees in any program that SEI would produce. But no start date nor intended test gas was provided. Mr. Parker did not present a report. He offered the lab fee information in direct response to my question. Bill Emy stated that ISEA and SEI were becoming separate entities, and that SEI has its own board of directors. He stated that he was not in a position to speak to SEI. He also stated that ISEA was not bound to use SEI as a certifier, but could use any certifier they choose to use. Bob Curtis of OSHA led the meeting, and he did not announce an SEI program. He did state that certification was not necessary for OSHA. If manufacturers could state that their product meets the ANSI standard requirements, and could provide the data, that was all that was necessary. If you believe that SEI's program was announced at that meeting, you have been misinformed.

I also cannot believe that SEI thought Sensidyne/Gastec to be uninterested in a passive monitor program. I relayed our interest to Mr. Augherton in numerous phone calls. I wrote a letter to Judith Bailey dated 9/30/94 with questions on the proposed program. Ms. Bailey answered some of the questions in a letter to me dated 12/1/94. My company spent nearly two thousand dollars to send me to the Salt Lake city meeting, and my name appeared in ISEA's meeting minutes. My letter of 2/3/95 regarding costs was written in an attempt to make both programs affordable to Gastec. How could SEI possibly conclude that we were not interested? All SEI had to do was ask. SEI was the party who knew that the testing was starting. We did not.

I have been involved in SEI's detector tube program since the initial "gathering interest" stage in 1984. SEI very skillfully handled the task of directing four strong competitors into one program. SEI acted as a "referee" and always made certain that the four companies were on a level playing field. There were many meetings and constant updates to manufacturers by telephone. A test schedule was published, and anyone who wanted to submit a product could do so. SEI's role as referee in this situation is very important to the manufacturers. In my opinion, if SEI no longer acts as referee, then SEI is no longer necessary. If clandestine certifications are allowed, the manufacturer might as well deal directly with the test lab and make his own claims.

You seem to be under the impression that SEI's name is an important issue with us. This is not necessarily true. SEI is still virtually unknown to the industrial hygienists. Our customers find out about SEI through our brochure. OSHA came to SEI as a result of a phone conversation I had with Rick Cee in June of 1991. At that time OSHA was conducting its own detector tube testing at the Salt Lake City lab. I told Rick about SEI's program in an attempt to reduce the duplication of effort. I gave him SEI's contact information. Prior to that time OSHA had little or no interest in SEI. Rick seemed to be completely unaware or at least uninterested in SEI's program. OSHA was already Sensidyne's customer, and had been since the 1970's when we were still Bendix. OSHA did not start using detector tubes as a result of the SEI program.

I see SEI's certification program for detector tubes as a benefit to the end user. I have this opinion because I worked as a field industrial hygienist for ten years. The management at Sensidyne and Gastec sees SEI's detector tube program as a cost of operation. We cannot point to any increased sales that can be attributed to SEI's program. We have remained in the tube program and planned to certify passive monitors, because as the SEI coordinator, I have

always advised Sensidyne and Gastec to participate as a service to end users. However, in light of recent developments with SEI, I am reconsidering this position.

Your letter of 6/6/95 does not address the direct questions I raised on the Envirometrics issue. It also does not address my proposed restart of the program under SEI's normal detector tube protocol. I have to assume that SEI has no intention of putting Envirometrics' formaldehyde certification on hold until others can be certified. If SEI does not intend to provide a level playing field, then I see no reason to pursue passive badge certification from SEI.

I am not in a position to make the final decision of participation for either Sensidyne or Gastec. However, as the SEI coordinator, I will advise both companies to pursue their own manufacturers' claims for passive badges by dealing directly with the laboratory. Instead of an SEI certification we would simply state, "Meets the requirements of ANSI Standard XXXX, validation study available upon request." If this is good enough for OSHA, it should be good enough for anyone.

As far as I know at this point, our detector tube certifications with SEI will remain unchanged. However, I believe there is a general lack of interest in this program among manufacturers, since we seem to be the lone participant submitting tubes for the new substances. If my proposed internal passive monitor program is accepted and successful, I will encourage a similar program in the future for our detector tubes. I believe such a program would be cost effective.

Again, I do not make the final decision on our participation in your passive monitor program. If SEI does eventually issue a test schedule, please copy me. I sincerely hope that SEI endeavors to improve communications with manufacturers in the future.

Sincerely,

Ron Roberson
Corporate Industrial Hygienist

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December 16, 1994

Patricia A Gleason, President
Safety Equipment Institute
1901 North Moore Street, Suite 808
Arlington, VA 22209

Dear Ms. Gleason:

Thank you for the opportunity to review the protocol you are considering for evaluating direct reading passive monitors, such as the ACT™ badges manufactured by Envirometrics Products Company. We are pleased that manufacturers of passive monitoring devices are considering funding the Safety Equipment Institute(SEI) to provide "third party certification" of the effectiveness of these devices. As you know, OSHA strongly supported the need for this type of verification in its recent expansion of the personal protective equipment standard (Ref. 29CFR1910.132, April 26, 1994). We also recognize the confidence manufacturers and government agencies, including NIOSH and MSHA, have demonstrated in SEI's ability to provide this service through their participation and comments regarding your existing certification programs. The success in your program to certify detector tubes is particularly noteworthy because it can be extended to cover what is needed for the certification of passive monitoring devices.

Published field studies indicate a large variability in workplace exposures. Therefore, we want to encourage employers to obtain multiple samples for varying working conditions to obtain a more realistic characterization of workplace exposures. The availability of effective, inexpensive, and easy to use devices, such as passive monitors, provides a needed resource to employers to achieve this objective. Unfortunately, our evaluations of early passive monitors identified problems with some of the devices on the market. The existence of a certification program to verify the claims of the manufacturers will greatly assist employers in identifying those devices which will be effective in monitoring their work sites. The program should also improve the overall quality of these devices as manufacturers strive to meet a higher "industry standard".

This brings us to the issue at hand. We recognize that the development of generic protocols for evaluating passive monitoring devices is being considered by both OSHA and ANSI. However, based on current knowledge, a successful evaluation of direct reading passive monitors by your protocol (as modified) would allow us to include the device as an option for use by OSHA compliance officers. Also, recognizing our common goal of providing employers with a variety of effective tools for evaluating workplace hazards, please let us know if we can be of assistance in reviewing specific protocols for other types of sampling devices.

Sincerely yours,

Robert A. Curtis, Director
OSHA Health Response Team

Rick Cee, Chief
Field Instruments Team

3M 110949

Protocol for the Evaluation of Direct Reading Passive Monitors

Introduction

The evaluation of passive devices should evaluate the manufacturer's claims of precision and accuracy over the range of operating conditions for which the devices are supposed to work. These conditions normally include but are not limited to concentration, temperature, relative humidity, face velocity, monitor orientation, reverse diffusion, exposure time, interferences, sampler stability, analytical variability, and shelf life. Recommended evaluation criteria for direct reading passive dosimeters are listed below.

In order to adequately evaluate the passive devices, the manufacturer must assure that the following exist: proper testing equipment and facilities; trained staff; written testing procedures; and calibration and quality control programs to perform the generation and testing of known concentrations in accordance with good industrial hygiene principles and practices.

General

The following are the elements for an evaluation of direct reading passive monitors, such as the ACT™ PEL-TWA and STEL monitoring cards (referred to only for example purposes). Unless otherwise stated, each exposure test should be conducted with 10 monitors for statistical analysis. Unless otherwise noted, standard exposure conditions apply to a temperature of 25 degrees Celsius, 50% relative humidity, 25 cm/s face velocity, specified exposure time of the monitor, and at the appropriate OSHA PEL or ACGIH TLV concentration for the analyte being tested.

Concentration and Exposure Time

Expose monitors to 0.5, 1.0 and 2.0 times the appropriate PEL or TLV and 1.0 time the OSHA ceiling or ACGIH STEL standard with 50% relative humidity at 25 degrees Celsius and a face velocity of 25 cm/s. PEL-TWA monitors are exposed for the maximum sampling time specified by the manufacturer. To determine whether any significant exposure exists in the workplace, a concentration of 0.1 times the appropriate PEL or TLV may be evaluated.

Relative Humidity

Expose monitors at the PEL or STEL concentration to 10 and 90 percent relative humidity at 25 degrees Celsius and 25 cm/s face velocity. For cards that have specified relative humidity ranges other than the typical 10 to 90 percent relative humidity, adjust the upper and lower humidity limits accordingly.

Temperature

Expose monitors at the appropriate PEL or TLV concentration with 50% relative humidity at 10 and 40 degrees Celsius for either eight hours or the appropriate ceiling or STEL sampling time. If a monitor has a specified temperature range other than the typical 10 to 40 degrees Celsius, the upper and lower temperature limits will be substituted in place of the 10 and 40 degrees Celsius exposures.

Pressure

Evaluate the adequacy of manufacturer's instructions for utilizing the monitoring devices for comparison to PEL and TLV concentrations at varying pressures, particularly due to changes in altitude.

Face Velocity

To determine the effects of face velocity, expose monitors to 10 and 150 cm/s at the appropriate PEL or TLV concentrations with 50% relative humidity at 25 degrees Celsius.

Interferences

Assess whether the manufacturer has adequately adressed potential positive and negative interferences based on the reaction chemistry used in the monitors. Where potential negative interferences have been documented in the literature, but have not been sufficiently evaluated by the manufacturer, the user manual will instruct the user to conduct initial side-by-side sampling with alternative methods to assess the amount of interference occurring at the specific work site, or the manual will explicitly state that the monitors can not be used in this type of environment.

Where interferences have been identified by the manufacturer, expose monitors to the interferences at their PEL for the maximum sampling time period. Document the extent of interferences observed.

Shelf Life

To verify shelf life, monitors will be stored per manufacturer's instructions (e.g. refrigerated if required by the user manual) and tested at standard conditions (i.e., 25 cm/s, 50% RH, PEL or TLV, and 25 Celsius) after the maximum stated shelf-life. Monitors may be given an initial certification based on an evaluation of manufacturer's tests of maximum shelf life.

Quality Control

Expose three different lots of monitors at standard concentration and exposure conditions to document the consistency between different manufactured lots.

Monitor Orientation

Expose monitors at orientations parallel and perpendicular to air flows of 10 and 150 cm/s at 1x PEL or TLV, 50%RH, and 25 Celsius.

Reverse Diffusion

Expose 20 monitors to a 2X exposure limit, 80% RH for 0.5X the maximum specified sampling time and to 0% exposure limit, 80% RH for 0.5X the maximum specified sampling time.

Inter-reader Variability

For direct reading dosimeters, inter-reader variability, either electronic or visual, must be assessed and incorporated into overall accuracy of the system.

Evaluation of Qualitative Monitors

A similar validation protocol to the quantitative monitors can be applied to qualitative monitors. Qualitative monitors are read visually by comparing the developed color to reference color guides provided on the card (some monitors have one reference guide). The color guides typically represent the action level and the PEL for PEL-TWA cards (8 hours). The color on the STEL or CEILING cards are based on the ACGIH STEL or OSHA CEILING standards respectively. The intensity of the developed color in relation to the color guide provides an indication of the exposure concentration.

PROPOSAL FOR AN INTEGRATED PROTOCOL

ANALYTICAL RECOVERY

4 samplers spiked at each of 4 levels (0.1, 0.5, 1.0, 2.0 x LV). 4 samplers spiked at 0.01 x LV (or method LOQ). 4 samplers pre-humidified and spiked with 1.0 x LV.

RATE AND CAPACITY

Samplers exposed to 2 x LV for 1,2,4,6, and 8 hours for TWA sampling (four samplers for each time-period), and to 1 x STEL for 15 minutes for STEL sampling (six samplers).

REVERSE DIFFUSION

NIOSH or CEN test using six samplers in each part (total 12).

STORAGE STABILITY

Track storage as per OSHA sample tube validations, e.g. 16 samplers exposed, 4 analyzed immediately, 4 samplers after 7, 14, and 21 days. Repeat refrigerated if sampler fails, or as routine.

WIND EFFECTS

Face velocity and orientation effects evaluated one time only with one analyte. Pressure can be evaluated at this stage.

TEMPERATURE EFFECTS

Separate to avoid difficult experimental conditions (80% rh @ 40°C), and correction factors confounding the factorial. Range can be chosen but stated clearly. Three experiments with 6 sampl rs each exposed to 2 x LV for 8 hours (ensures no reverse diffusion at high temps) at low, medium and high temperatures (18 samplers).

FACTORIAL

Should include concentration, exposure time, humidity, and interference (four samplers in each of 8 experiments).

SHELF LIFE

Repeat rate/capacity at expiration.

ACCURACY & PRECISION

To be discussed.

3M Occupational Health and
Environmental Safety Division

3M Center
St. Paul, MN 55144-1000
612 733 1110

Dan

November 10, 1994

Pat Gleason
Safety Equipment Institute
1901 North Moore Street
Arlington, VA 22209

Dear Ms. Gleason:

It was a pleasure talking with you about validating/certifying diffusion monitors. We are very pleased that SEI has decided to pursue this issue and help in the development of an ANSI committee that will write a performance protocol for diffusion monitors. We are excited about the opportunity to work with SEI and ANSI on this program.

I have reviewed the draft protocol that you sent. In general, it covers most of the important performance parameters and it will be a good guideline to build upon. My comments are as follows:

Introduction

I realize that this draft document was written for direct reading passive sampling devices and that the accuracy of greater than 50% may be acceptable for such devices, however, we believe that the diffusion monitor has to be more accurate. The protocol for the diffusion monitor should address the traditional plus or minus 25% accuracy at a confidence level of 95%. The main purpose for developing a protocol is to show the health and safety professional that diffusion monitors are just as accurate as active sampling techniques. The protocol needs to convey to the user the limitations and operating range of the sampling device. Another area that needs to be addressed, is the need to certify for each compound verses a certification for an entire class of compounds. Reference to operating temperature should include some allowance for variability, such as 25°C ± 3°C.

Concentrations and Exposure Time

The main purpose of this experiment is to determine the sampling limitations of the diffusion monitor. It will evaluate the linear sampling rate and capacity of the device. We believe a factorial design with three concentration ranges such as 0.5 x EL, 1 x EL and 2 x EL vs. 30, 120 and 480 minute sampling times might give the user more information than the outlined experiment. This design would give the user a range of operating concentrations and times instead of a single operating concentration and time. The manufacturer would have to state their operating conditions and the certification protocol would serve to verify these conditions.

Relative Humidity

This experiment did not contain any end-point to measure performance. The test protocol needs to have these targets established. The humidities of 10% and 90% are not realistic to most workplaces. We recommend using the humidities of 30% and 80%.

Temperature

Temperature will influence the sampling rate of the diffusion monitor. The manufacturer should show correction factors for temperature ranges. It has been our experience that these corrections are very small and that if the experiment is not carefully controlled and designed, the sampling and analytical error would mask any deviation due to temperature changes.

Pressure

We believe that pressure will not influence the overall performance of the diffusion monitor, therefore a designed experiment is not necessary.

Reverse Diffusion

Reverse diffusion measures the ability of the sorbent to hold onto the analyte. Typically sampling device overloading is one of the most common errors made in

use of either active or passive sampling devices and can significantly contribute to inaccurate air measurements. The outlined experiment does not include any statistically performance criteria.

Sampling Rate, Analytical Recovery & Storage

These performance parameters were absent and will have to be addressed in the protocol.

I want to thank you for allowing 3M to comment on this first draft. It is our opinion that the draft needs more work on addressing sample sizes and statistics, plus defining final performance criteria. However, we believe that you have touched on all the important performance parameters. We are drafting a similar document that consolidates the NIOSH and European protocols, plus draws on our own knowledge. We would be happy to share this document with you when it is completed. 3M would like to actively be involved with the entire development of this protocol so please keep us updated. I look forward to working with you and SEI on this program. If you have any questions, please feel free to contact me at 612-737-4459.

Best regards,

RAWeber

Robert A. Weber, CIH
Sr. Technical Service Representative
3M Occupational Health & Environmental Safety Division

RAW:llj/172

October 24, 1994

Patricia A Gleason, President
Safety Equipment Institute
1901 North Moore Street, Suite 808
Arlington, VA 22209

Dear Ms. Gleason:

Thank you for the opportunity to review the protocol you are considering for evaluating direct reading passive monitors, such as the ACT™ badges manufactured by Envirometrics Products Company. We are pleased that manufacturers of passive monitoring devices are considering funding the Safety Equipment Institute(SEI) to provide "third party certification" of the effectiveness of these devices. As you know, OSHA strongly supported the need for this type of verification in its recent expansion of the personal protective equipment standard (Ref. 29CFR1910.132, April 26, 1994). We also recognize the confidence manufacturers and government agencies, including NIOSH and MSHA, have demonstrated in SEI's ability to provide this service through their participation and comments regarding your existing certification programs. The success in your program to certify detector tubes is particularly noteworthy since it parallels what we envision is needed for the certification of passive monitoring devices.

Recent literature and data from NIOSH field studies indicate that the variability in workplace exposure is often much greater than the variability in sampling. Therefore, we want to encourage employers to obtain multiple samples for varying working conditions to obtain a more realistic characterization of workplace exposures. The availability of effective, inexpensive, and easy to use devices, such as passive monitors, provides a needed resource to employers to achieve this objective. Unfortunately, our evaluations of early passive monitors identified problems with some of the devices on the market. The existence of a certification program to verify the claims of the manufacturers will greatly assist employers in identifying those devices which will be effective in monitoring their work sites. The program should also improve the overall quality of these devices as manufacturers strive to meet a higher "industry standard".

This brings us to the issue at hand. We recognize that the development of generic protocols for evaluating passive monitoring devices is being considered by both OSHA and NIOSH. However, based on current knowledge, a successful evaluation of direct reading passive monitors by your protocol (as modified) would allow us to include the device as an option for use by OSHA compliance officers. Also, recognizing our common goal of providing employers with a variety of effective tools for evaluating workplace hazards, please let us know if we can be of assistance in reviewing specific protocols for other types of sampling devices.

Sincerely yours,

Robert A. Curtis
Director, OSHA Health Response Team

SEI Protocol for the Evaluation of Direct Reading Passive Monitors
DRAFT - 10/24/94

Introduction

The evaluation of passive devices should evaluate the manufacturer's claims of precision and accuracy over the range of operating conditions for which the devices are supposed to work. These conditions normally include but are not limited to concentration, temperature, relative humidity, face velocity, monitor orientation, reverse diffusion, exposure time, interferences, sampler stability, and shelf life. Recommended evaluation criteria for direct reading passive dosimeters are listed below.

Traditionally, the goal of an acceptable monitoring method was to ensure an accuracy, to a 95% confidence level, of not less than plus or minus 25% at concentrations of contaminant at the occupational exposure limits (OSHA PEL's, ACGIH TLV's). The NIOSH protocol for evaluating sampling and analytical procedures attempts to verify the achievement of this goal over a range of exposure conditions. However, devices which do not meet the NIOSH criteria can still provide equivalent or better worker protection under the following conditions:

1) The manufacturer expressly states the conditions under which the monitors do meet the validation criteria. For example, although draft NIOSH criteria for temperature effects require validation at 10, 25, and 40 degrees C, a large number of employee exposures occur in a much narrower temperature range, particularly in indoor operations. Therefore, if a device does not meet the accuracy criteria over a broad temperature range, the manufacturer may narrow the operating temperature range specified in its user manual to that range for which the criteria are met.

2) Methods with greater imprecision or inaccuracy may be acceptable if either 1) an adequate number of samples are collected by the user to characterize the distribution of employee exposures to the same level of statistical confidence that employee exposures comply with occupational standards, or 2) a positive error correction is made by the user to determine the potential upper level of exposure as long as the error corrections do not exceed the following values:

   - The inaccuracy at 0.5X, 1.0X, or 2.0X of the PEL or TLV does not exceed +/- 50% of the true concentration 95% of the time.

   - The inaccuracy at 0.1X the PEL or TLV does not exceed +/- 100% of the true concentration 95% of the time.

   - The inaccuracy at 1.0X the OSHA ceiling or ACGIH STEL does not exceed +/- 50% the true concentration 95% of the time.

In order to adequately evaluate the passive devices, the manufacturer must assure that the following exist: proper testing equipment and facilities; trained staff; written testing procedures; and calibration and quality control programs to perform the generation and testing of known concentrations in accordance with good industrial hygiene principles and practices.

General

The following are the elements for an evaluation of direct reading passive monitors, such as the ACT™ PEL-TWA and STEL monitoring cards (referred to only for example purposes). Unless otherwise stated, each exposure test should be conducted with 10 monitors for statistical analysis. Unless otherwise noted, standard exposure conditions apply to a temperature of 25 degrees Celsius, 50% relative humidity, 25 cm/s face velocity, specified exposure time of the monitor, and at the appropriate OSHA PEL or ACGIH TLV concentration for the analyte being tested.

Concentration and Exposure Time

Expose monitors to 0.5, 1.0 and 2.0 times the appropriate PEL or TLV and 1.0 time the OSHA ceiling or ACGIH STEL standard with 50% relative humidity at 25 degrees Celsius and a face velocity of 25 cm/s. PEL-TWA monitors are exposed for the maximum sampling time specified by the manufacturer. To determine whether any significant exposure exists in the workplace, a concentration of 0.1 times the appropriate PEL or TLV may be evaluated.

Relative Humidity

Expose monitors at the PEL or STEL concentration to 10 and 90 percent relative humidity at 25 degrees Celsius and 25 cm/s face velocity. For cards that have specified relative humidity ranges other than the typical 10 to 90 percent relative humidity, adjust the upper and lower humidity limits accordingly.

Temperature

Expose monitors at the appropriate PEL or TLV concentration with 50% relative humidity at 10 and 40 degrees Celsius for either eight hours or the appropriate ceiling or STEL sampling time. If a monitor has a specified temperature range other than the typical 10 to 40 degrees Celsius, the upper and lower temperature limits will be substituted in place of the 10 and 40 degrees Celsius exposures.

Pressure

Evaluate the adequacy of manufacturer's instructions for utilizing the monitoring devices for comparison to PEL and TLV concentrations at varying pressures, particularly due to changes in altitude.

Face Velocity

To determine the effects of face velocity, expose monitors to 10 and 150 cm/s at the appropriate PEL or TLV concentrations with 50% relative humidity at 25 degrees Celsius.

Interferences

Assess whether the manufacturer has adequately adressed potential positive and negative interferences based on the reaction chemistry used in the monitors. Where potential negative interferences have been documented in the literature, but have not been sufficiently evaluated by the manufacturer, the user manual will instruct the user to conduct initial side-by-side sampling with alternative methods to assess the amount of interference occurring at the specific work site, or the manual will explicitly state that the monitors can not be used in this type of environment.

Where interferences have been identified by the manufacturer, expose monitors to the interferences at their PEL for the maximum sampling time period. Document the extent of interferences observed.

Shelf Life

To verify shelf life, monitors will be stored per manufacturer's instructions (e.g. refrigerated if required by the user manual) and tested at standard conditions (i.e., 25 cm/s, 50% RH, PEL or TLV, and 25 Celsius) after the maximum stated shelf-life. Monitors may be given an initial certification based on an evaluation of manufacturer's tests of maximum shelf life.

Quality Control

Expose three different lots of monitors at standard concentration and exposure conditions to document the consistency between different manufactured lots.

Monitor Orientation

Expose monitors at orientations parallel and perpendicular to air flows of 10 and 150 cm/s at 1x PEL or TLV, 50%RH, and 25 Celsius.

Reverse Diffusion

Expose 20 monitors to a 2X exposure limit, 80% RH for 0.5X the maximum specified sampling time and to 0% exposure limit, 80% RH for 0.5X the maximum specified sampling time.

Inter-reader Variability

For direct reading dosimeters, inter-reader variability, either electronic or visual, must be assessed and incorporated into overall accuracy of the system.

Evaluation of Qualitative Monitors

A similar validation protocol to the quantitative monitors can be applied to qualitative monitors. Qualitative monitors are read visually by comparing the developed color to reference color guides provided on the card (some monitors have one reference guide). The color guides typically represent the action level and the PEL for PEL-TWA cards (8 hours). The color on the STEL or CEILING cards are based on the ACGIH STEL or OSHA CEILING standards respectively. The intensity of the developed color in relation to the color guide provides an indication of the exposure concentration.

October 24, 1994

Patricia A Gleason, President
Safety Equipment Institute
1901 North Moore Street, Suite 808
Arlington, VA 22209

Dear Ms. Gleason:

Thank you for the opportunity to review the protocol you are considering for evaluating direct reading passive monitors, such as the ACT™ badges manufactured by Envirometrics Products Company. We are pleased that manufacturers of passive monitoring devices are considering funding the Safety Equipment Institute(SEI) to provide "third party certification" of the effectiveness of these devices. As you know, OSHA strongly supported the need for this type of verification in its recent expansion of the personal protective equipment standard (Ref. 29CFR1910.132, April 26, 1994). We also recognize the confidence manufacturers and government agencies, including NIOSH and MSHA, have demonstrated in SEI's ability to provide this service through their participation and comments regarding your existing certification programs. The success in your program to certify detector tubes is particularly noteworthy since it parallels what we envision is needed for the certification of passive monitoring devices.

Recent literature and data from NIOSH field studies indicate that the variability in workplace exposure is often much greater than the variability in sampling. Therefore, we want to encourage employers to obtain multiple samples for varying working conditions to obtain a more realistic characterization of workplace exposures. The availability of effective, inexpensive, and easy to use devices, such as passive monitors, provides a needed resource to employers to achieve this objective. Unfortunately, our evaluations of early passive monitors identified problems with some of the devices on the market. The existence of a certification program to verify the claims of the manufacturers will greatly assist employers in identifying those devices which will be effective in monitoring their work sites. The program should also improve the overall quality of these devices as manufacturers strive to meet a higher "industry standard".

This brings us to the issue at hand. We recognize that the development of generic protocols for evaluating passive monitoring devices is being considered by both OSHA and NIOSH. However, based on current knowledge, a successful evaluation of direct reading passive monitors by your protocol (as modified) would allow us to include the device as an option for use by OSHA compliance officers. Also, recognizing our common goal of providing employers with a variety of effective tools for evaluating workplace hazards, please let us know if we can be of assistance in reviewing specific protocols for other types of sampling devices.

Sincerely yours,

Robert A. Curtis
Director, OSHA Health Response Team

SEI Protocol for the Evaluation of Direct Reading Passive Monitors
DRAFT - 10/24/94

Introduction

The evaluation of passive devices should evaluate the manufacturer's claims of precision and accuracy over the range of operating conditions for which the devices are supposed to work. These conditions normally include but are not limited to concentration, temperature, relative humidity, face velocity, monitor orientation, reverse diffusion, exposure time, interferences, sampler stability, and shelf life. Recommended evaluation criteria for direct reading passive dosimeters are listed below.

Traditionally, the goal of an acceptable monitoring method was to ensure an accuracy, to a 95% confidence level, of not less than plus or minus 25% at concentrations of contaminant at the occupational exposure limits (OSHA PEL's, ACGIH TLV's). The NIOSH protocol for evaluating sampling and analytical procedures attempts to verify the achievement of this goal over a range of exposure conditions. However, devices which do not meet the NIOSH criteria can still provide equivalent or better worker protection under the following conditions:

NIOSH protocol overkill

1) The manufacturer expressly states the conditions under which the monitors do meet the validation criteria. For example, although draft NIOSH criteria for temperature effects require validation at 10, 25, and 40 degrees C, a large number of employee exposures occur in a much narrower temperature range, particularly in indoor operations. Therefore, if a device does not meet the accuracy criteria over a broad temperature range, the manufacturer may narrow the operating temperature range specified in its user manual to that range for which the criteria are met.

2) Methods with greater imprecision or inaccuracy may be acceptable if either 1) an adequate number of samples are collected by the user to characterize the distribution of employee exposures to the same level of statistical confidence that employee exposures comply with occupational standards, or 2) a positive error correction is made by the user to determine the potential upper level of exposure as long as the error corrections do not exceed the following values:

are you allowing not monitors that are typically accurate? Confusing

- The inaccuracy at 0.5X, 1.0X, or 2.0X of the PEL or TLV does not exceed +/- 50% of the true concentration 95% of the time.

too high

- The inaccuracy at 0.1X the PEL or TLV does not exceed +/- 100% of the true concentration 95% of the time.

- The inaccuracy at 1.0X the OSHA ceiling or ACGIH STEL does not exceed +/- 50% the true concentration 95% of the time.

- not all experiments look @ evaluating structural classes
- Missing info on Sampling Rate

In order to adequately evaluate the passive devices, the manufacturer must assure that the following exist: proper testing equipment and facilities; trained staff; written testing procedures; and calibration and quality control programs to perform the generation and testing of known concentrations in accordance with good industrial hygiene principles and practices.

General

The following are the elements for an evaluation of direct reading passive monitors, such as the ACT™ PEL-TWA and STEL monitoring cards (referred to only for example purposes). Unless otherwise stated, each exposure test should be conducted with 10 monitors for statistical analysis. Unless otherwise noted, standard exposure conditions apply to a temperature of 25 degrees Celsius, 50% relative humidity, 25 cm/s face velocity, specified exposure time of the monitor, and at the appropriate OSHA PEL or ACGIH TLV concentration for the analyte being tested.

Concentration and Exposure Time (Factorial Design)

Expose monitors to 0.5, 1.0 and 2.0 times the appropriate PEL or TLV and 1.0 time the OSHA ceiling or ACGIH STEL standard with 50% relative humidity at 25 degrees Celsius and a face velocity of 25 cm/s. PEL-TWA monitors are exposed for the maximum sampling time specified by the manufacturer. To determine whether any significant exposure exists in the workplace, a concentration of 0.1 times the appropriate PEL or TLV may be evaluated.

Relative Humidity

Expose monitors at the PEL or STEL concentration to 10 and 90 percent relative humidity at 25 degrees Celsius and 25 cm/s face velocity. For cards that have specified relative humidity ranges other than the typical 10 to 90 percent relative humidity, adjust the upper and lower humidity limits accordingly.

Temperature

Expose monitors at the appropriate PEL or TLV concentration with 50% relative humidity at 10 and 40 degrees Celsius for either eight hours or the appropriate ceiling or STEL sampling time. If a monitor has a specified temperature range other than the typical 10 to 40 degrees Celsius, the upper and lower temperature limits will be substituted in place of the 10 and 40 degrees Celsius exposures.

Pressure

Evaluate the adequacy of manufacturer's instructions for utilizing the monitoring devices for comparison to PEL and TLV concentrations at varying pressures, particularly due to changes in altitude.

$\frac{10\ cm}{sec}\left(\frac{1\ m}{100\ cm}\right)\left(\frac{3\ ft}{1\ m}\right)\frac{60}{min}$: ft/min

~~50 ft~~ -25

20-25 ft/min to ~~50 ft~~ 200 ft/min

Face Velocity

To determine the effects of face velocity, expose monitors to 10 and 150 cm/s at the appropriate PEL or TLV concentrations with 50% relative humidity at 25 degrees Celsius.

10 x

Interferences - ~~does not need to coincide w/ PEL~~

Assess whether the manufacturer has adequately adressed potential positive and negative interferences based on the reaction chemistry used in the monitors. Where potential negative interferences have been documented in the literature, but have not been sufficiently evaluated by the manufacturer, the user manual will instruct the user to conduct initial side-by-side sampling with alternative methods to assess the amount of interference occurring at the specific work site, or the manual will explicitly state that the monitors can not be used in this type of environment.

Where interferences have been identified by the manufacturer, expose monitors to the interferences at their PEL for the maximum sampling time period. Document the extent of interferences observed.

Shelf Life

To verify shelf life, monitors will be stored per manufacturer's instructions (e.g. refrigerated if required by the user manual) and tested at standard conditions (i.e., 25 cm/s, 50% RH, PEL or TLV, and 25 Celsius) after the maximum stated shelf-life. Monitors may be given an initial certification based on an evaluation of manufacturer's tests of maximum shelf life.

Quality Control

Expose three different lots of monitors at standard concentration and exposure conditions to document the consistency between different manufactured lots.

Monitor Orientation

Expose monitors at orientations parallel and perpendicular to air flows of 10 and 150 cm/s at 1x PEL or TLV, 50%RH, and 25 Celsius.

Reverse Diffusion

~~Expose 20~~ monitors to a 2X exposure limit, 80% RH for 0.5X the maximum specified sampling time and to 0% exposure limit, 80% RH for 0.5X the maximum specified ~~sampling~~ time.

- ~~NEL~~
- No end point
- No performance data
- Small

2 EL

Reverse diffusion

~~This test~~ ~~The overall~~ - ~~This test does not have~~

Reverse diffusion ~~is a~~ ~~is the capacity of the DM has been reached~~ measure the ability of the ~~DM~~ sorbent to hold onto the analyte

This ~~test~~ optional test ~~did~~ does not ~~make any~~ include or ~~state~~ statement ~~in~~ performance criteria.

Inter-reader Variability

For direct reading dosimeters, inter-reader variability, either electronic or visual, must be assessed and incorporated into overall accuracy of the system.

Evaluation of Qualitative Monitors

A similar validation protocol to the quantitative monitors can be applied to qualitative monitors. Qualitative monitors are read visually by comparing the developed color to reference color guides provided on the card (some monitors have one reference guide). The color guides typically represent the action level and the PEL for PEL-TWA cards (8 hours). The color on the STEL or CEILING cards are based on the ACGIH STEL or OSHA CEILING standards respectively. The intensity of the developed color in relation to the color guide provides an indication of the exposure concentration.

~~3~~ Sample Rate

~~the~~ This ~~was~~ was absent + it ~~will~~ will have to be performance included in the protocol.

I want to thank you for allowing 3M to comment on this ~~draft~~ first draft. ~~and to participate~~ It is our opinion that it ~~will~~ needs a considerable amount of work, ~~before~~ ~~but~~ w/respect to defining final performance criteria; however, we ~~believe~~ believe that you have touched on ~~the~~ all the important performance parameters. We are in the middle of drafting a similar document that consolidates ~~our~~ the NIOSH, CEN + our own opinions

TECHNIQUE FOR DETERMINING CAPACITY OF DIFFUSIONAL SAMPLING DEVICES

And rs, L. W., Occupational Health & Safety Products Division, 3M Coapany, Saint Paul, Minnesota 55144.

ABSTRACT

Diffusional sampling is a very convanient technique for measuring the concentration of potentially hazardous or toxic gases and vapors in an environment. In this technique, as dafined by Fick's Law of Diffusion, the contaminant molecules diffuse from the aabient atmosphere to the activated carbon adsorbent because of the concentration gradient between the aabient and tha adsorbent. The contaminant concentration must be zero or near zero at the adsorbent layer for the sampling rate to be function only of the ambient concentration. There is a limit to this criteria because the adsorbent has a finite capacity for a contaminant. During sampling, the weight of contaminant collected must not exceed the adsorbent's capacity and, therefore, the diffusional sampling limits.

The adsorbent's capacity for a contaminant in diffusional sampling device can be determined by spiking an excess of the contaminant onto a set of monitors. During an exposure of these monitors to a challenge with zero concentration of the contaminant, the amount of contaminent lost by the adsorbent as a function of time can be determined by the s quential removal and analysis of the monitor. The contaminant loss asymptotically approaches a limiting value, the adsorbent's capacity for the contaminant. For most common contaminants, the adsorbent's capacity can be expressed as a linear function of the contaminant's boiling point.

TECHNIQUE FOR DETERMINING CAPACITY OF DIFFUSIONAL SAMPLING DEVICES

Anders, L. W., Occupational Health & Safety Products Division,
3M Company, Saint Paul, Minnesota 55144

INTRODUCTION

Diffusional sampling is a very simple technique for collecting potentially hazardous or toxic gases and vapors from the ambient environment. For these devices, the sampling rate is controlled by diffusion and sample collection by absorption or chemical reaction. With a diffusional device, the contaminant is sampled from the ambient atmosphere in the absence of air flow. This is in contrast to the conventional charcoal tubes where the sampling rate is determined by the air flow rate of a mechanical pump. With a diffusional sampling device, the sampling rate is defined by Fick's Law where the weight collected is directly proportional to the concentration of the contaminant in the ambient atmosphere, the sampling time and a proportionality constant (DA/L) assuming $C_o = 0$.

$$W = \frac{DA}{L} (C-C_o)\, t \qquad (1)$$

By combining the units f r the diffusional coeffici nt (cm^2/min.) for the contaminant, the geometric area (cm^2) and geometric length (cm) of the diffusional chamber, it can be observed that the proportionality constant haa units of cubic centimeters per minute (cm^3/min.).

$$K = \frac{DA}{L} \qquad (2)$$

Therefore, equation (1) can be simplified to the following:

$$W = K\,(C-C_o)\,t \qquad (3)$$

It is usually assumed that the concentration (C_o) at the adsorbent layer is zero or nearly zero. This is an important criteria and when it fails, diffusional sampling is not easily defined by the above integrated form of Fick's Law. Not only is the concentration (C) in the ambient atmosphere an unknown, but the concentration (C_o) at the adsorbent is also an unknown. Therefore, the adsorbent is responsible for effectively collecting the contaminant and maintaining a concentration (C_o) equal to or nearly equal to zero. The adsorbent is able to maintain this requirement until its capacity is reached and then the diffusional sampling limits have been exceeded.

Procedure

A technique has been developed to determine the capacity of the activated carbon in the 3M Organic Vapor Monitor. After spiking a set of monitors with an excess of a contaminant, they are exposed to an air

flow with zero concentration of the contaminant. At various time intervals monitors are removed and analyzed. The amount of contaminant on the monitor is plotted as function of time. By this technique, initially, the adsorbent contains more contaminant than it can effectively collect and hold during the sampling process. The capacity for the contaminant is determined from the limiting value which is asymptotically approached at infinite time. In a diffusional sampling device, the adsorbent can effectively collect and hold the contaminant as long as this capacity is not exceeded.

Results and Discussion

A set of monitors were overloaded with 49.5 milligrams and with 20.5 milligrams of methyl ethyl ketone according to the spiking procedure outlined for determination of recovery coefficients for the 3M Organic Vapor Monitors. These monitors were placed in a device with an air challenge containing zero concentration of methyl ethyl ketone. As shown in Figure 1, the amount of methyl ethyl ketone adsorbed strongly on the activated carbon asymptotically approaches a limiting value. These relationships can be transformed into linear functions as shown in Figure 2 where the reciprocal of the weight loss ($1/W_o-W_1$) is plotted as a function of the reciprocal of the time ($1/t$). It can be observed the data fits the following linear relationship

$$\frac{1}{W_o-W_1} = b + m\frac{1}{t} \qquad (4)$$

It can be observed that as the time (t) approaches infinity, the value

It can be observed that as the time (t) approaches infinity, the value of the reciprocal of the time approaches zero and $W_i = W_c$. Therefore, from the value of the intercept (b), the capacity (W_c) can readily be determined by the following relationship -

$$W_c = W_o - \frac{1}{b} \qquad (5)$$

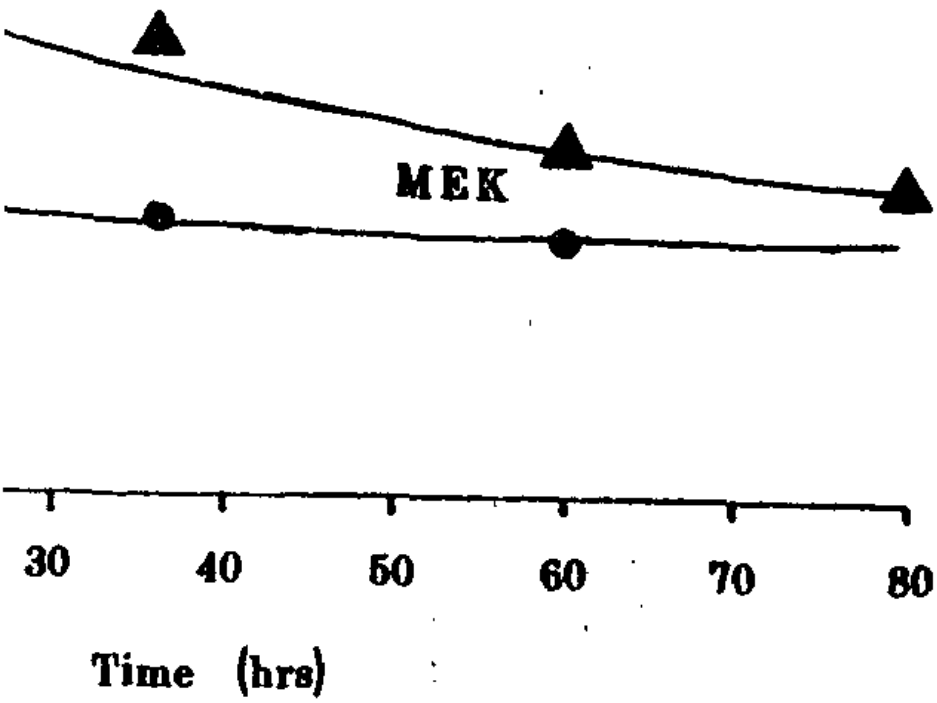
In Figure 1, it can be observed that both overload levels are asymptotically approaching the same limiting value. From the intercept values, the capacity of the adsorbent in the 3M Organic Vapor Monitor is determined to be 12.4 milligrams for methyl ethyl ketone.

The activated carbon should have a unique capacity for every contaminant which is dependent on the heat of adsorption. In Figure 3, it can be observed that for a group of ketones the activated carbon has a different capacity for each. These relationships were transformed into linear functions along with numerous other contaminants. As depicted in Figure 4, the capacity can be plotted as a function of the contaminant boiling point. It can be observed that the activated carbon has approximately the same relationship between capacity and boiling point for most contaminants except for the aliphatic compounds which have a relationship with somewhat greater capacity for the lower boiling point compounds.

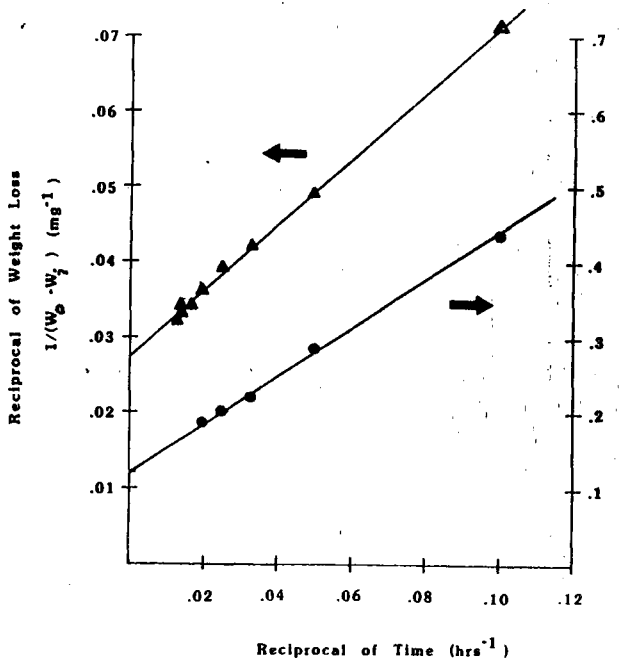
From Figure 5, the necessary capacity required for sampling any contaminant with the 3M Organic Vapor Monitor can be determined. Assuming the contaminant concentration in the environment is at the

p rmissible exposure level (PEL) and if an eight hour sampling period is desired, then the amount f o ntaminant collected by the 3M Organic Vapor Monitor can readily be determined from the relationship plotted in Figure 5. For many of the frequently sampled contaminants, the required capacities when sampling at the PEL for eight hours are plotted in Figure 6. As can be observed in Figure 6, the activated carbon in the 3M Organic Vapor Monitor has sufficient capacities to sample eight hours at the PEL for those contaminants with boiling points of 90°C or greater. These account for 70% of the most fr quently sampled contaminants. An additional 20% of the contaminants have boiling points in the range from 60°C to 90°C. For these contaminants, when sampling at concentration near the PEL, it is recommended that the sampling period be shortened to a three to six hour period depending on the concentration. The final 10% of the most frequently sampled contaminants have boiling points below 60°C and must have the length of the sampling period selected according to the contaminant concentration.

DETERMINATION
OF
ADSORBENT CAPACITY



ADSORBENT CAPACITY OF MEK



CAPACITY DETERMINATION

$$\frac{1}{w_o - w_i} = b + m\frac{1}{t}$$

CAPACITY DETERMINATION

$$\frac{1}{w_o - w_i} = b + m\,\frac{1}{t}$$

As $t \rightarrow \infty$

$$w_i = w_c$$

CAPACITY DETERMINATION

$$\frac{1}{w_o - w_i} = b + m\,\frac{1}{t}$$

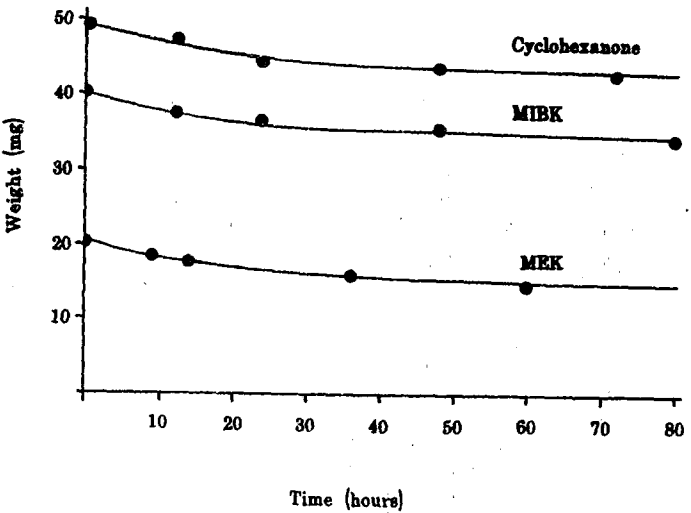
As $t \rightarrow \infty$

$$w_i = w_c$$

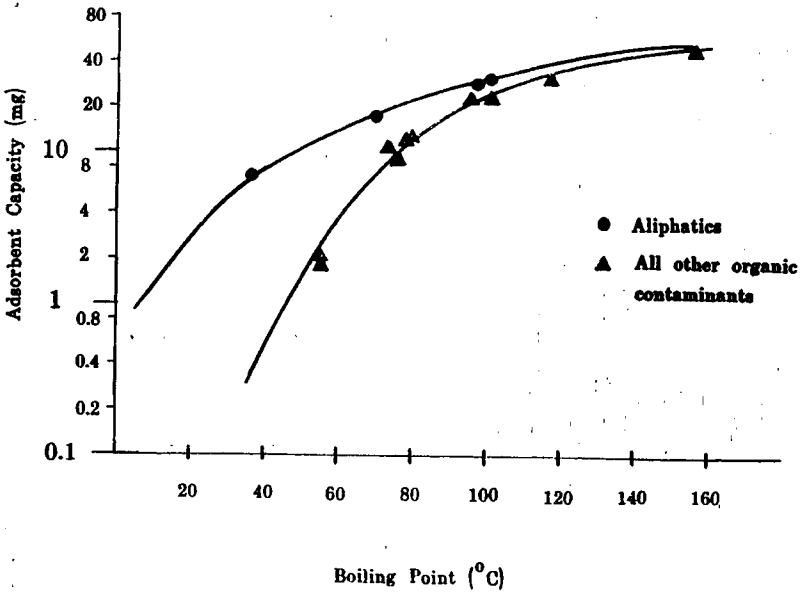
Then

$$w_c = w_o - \frac{1}{b}$$

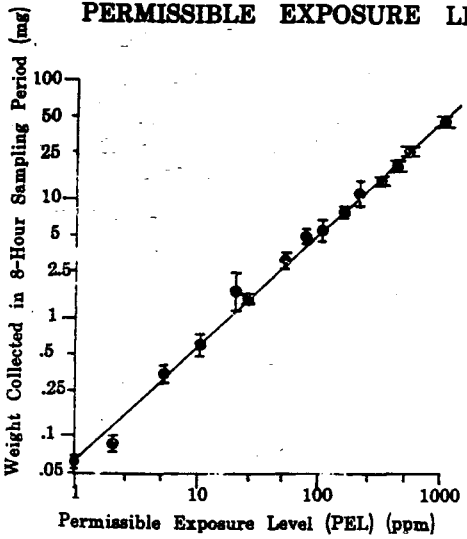
DETERMINATION OF ADSORBENT CAPACITY



ADSORBENT CAPACITY AS A FUNCTION OF BOILING POINT OF CONTAMINANT

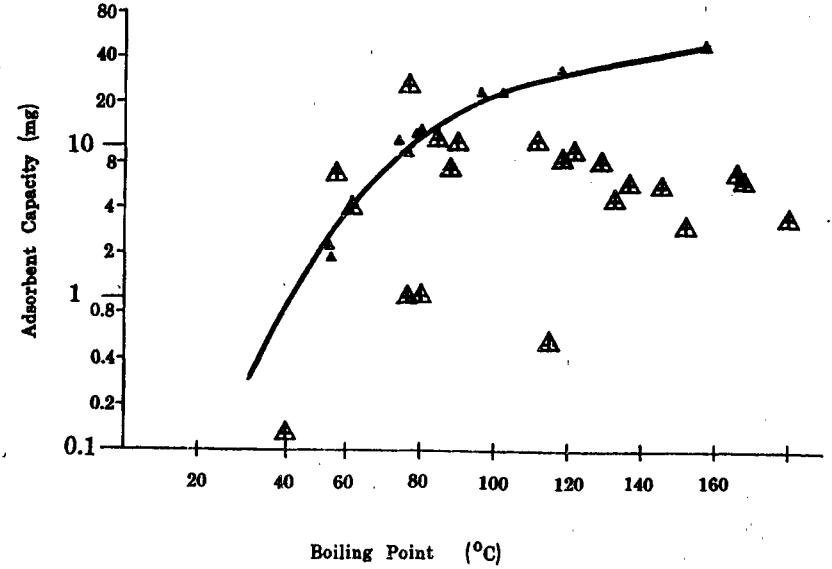


WEIGHT COLLECTED AS A FUNCTION OF PERMISSIBLE EXPOSURE LEVEL

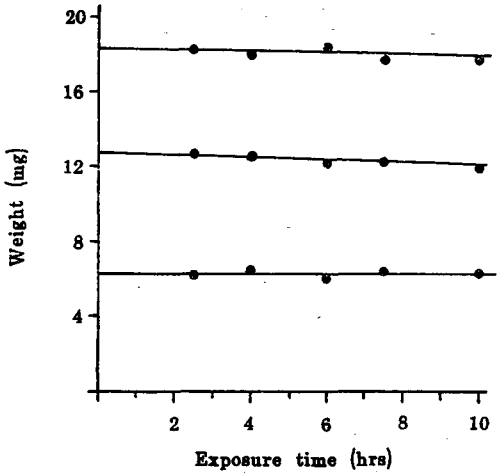


3M 111020

ADSORBENT CAPACITY AS A FUNCTION OF BOILING POINT OF CONTAMINANT



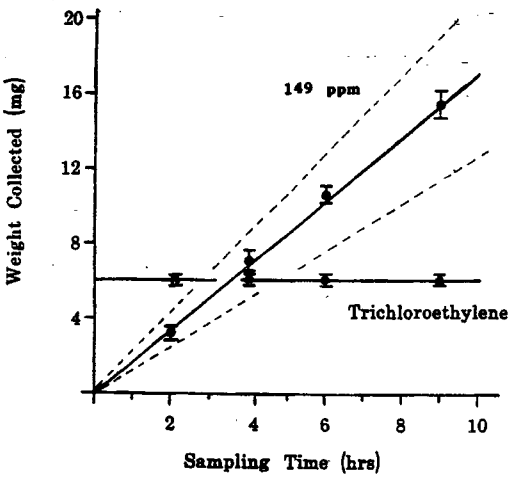
MONITOR RETENTION OF PRELOADED TRICHLOROETHYLENE WHEN EXPOSED TO AIR AT 85% RH



3M 111022

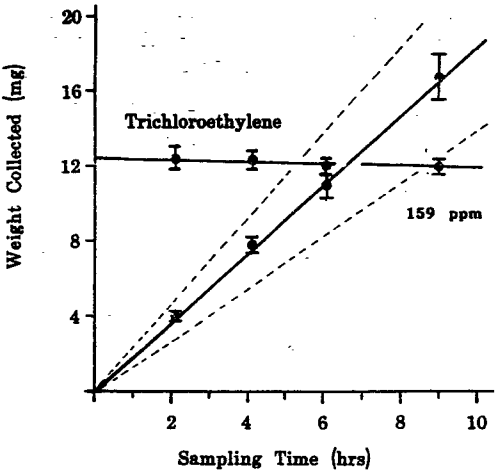
SAMPLING PERCHLOROETHYLENE WITH MONITORS PRELOADED WITH TRICHLOROETHYLENE

85% - RH



SAMPLING PERCHLOROETHYLENE WITH MONITORS PRELOADED WITH TRICHLOROETHYLENE

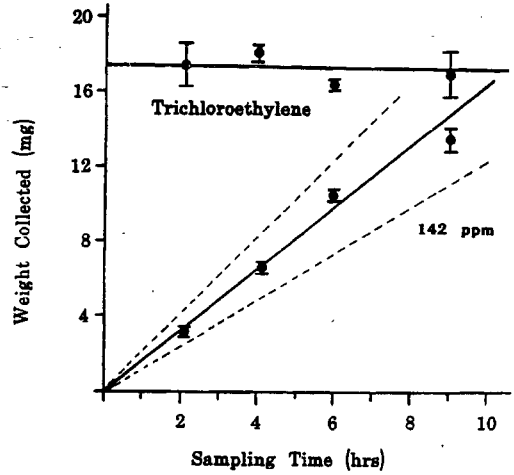
85% - RH



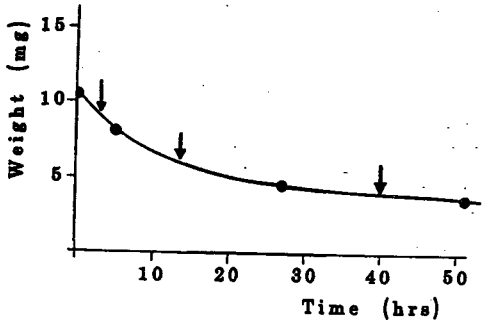
3M 111024

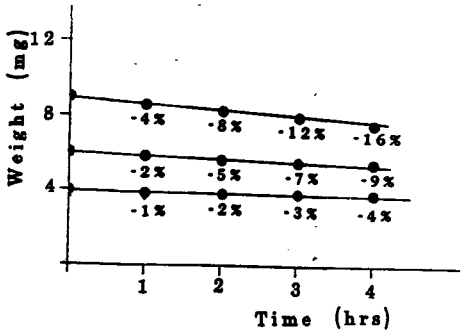
SAMPLING PERCHLOROETHYLENE WITH MONITORS PRELOADED WITH TRICHLOROETHYLENE

85% - RH



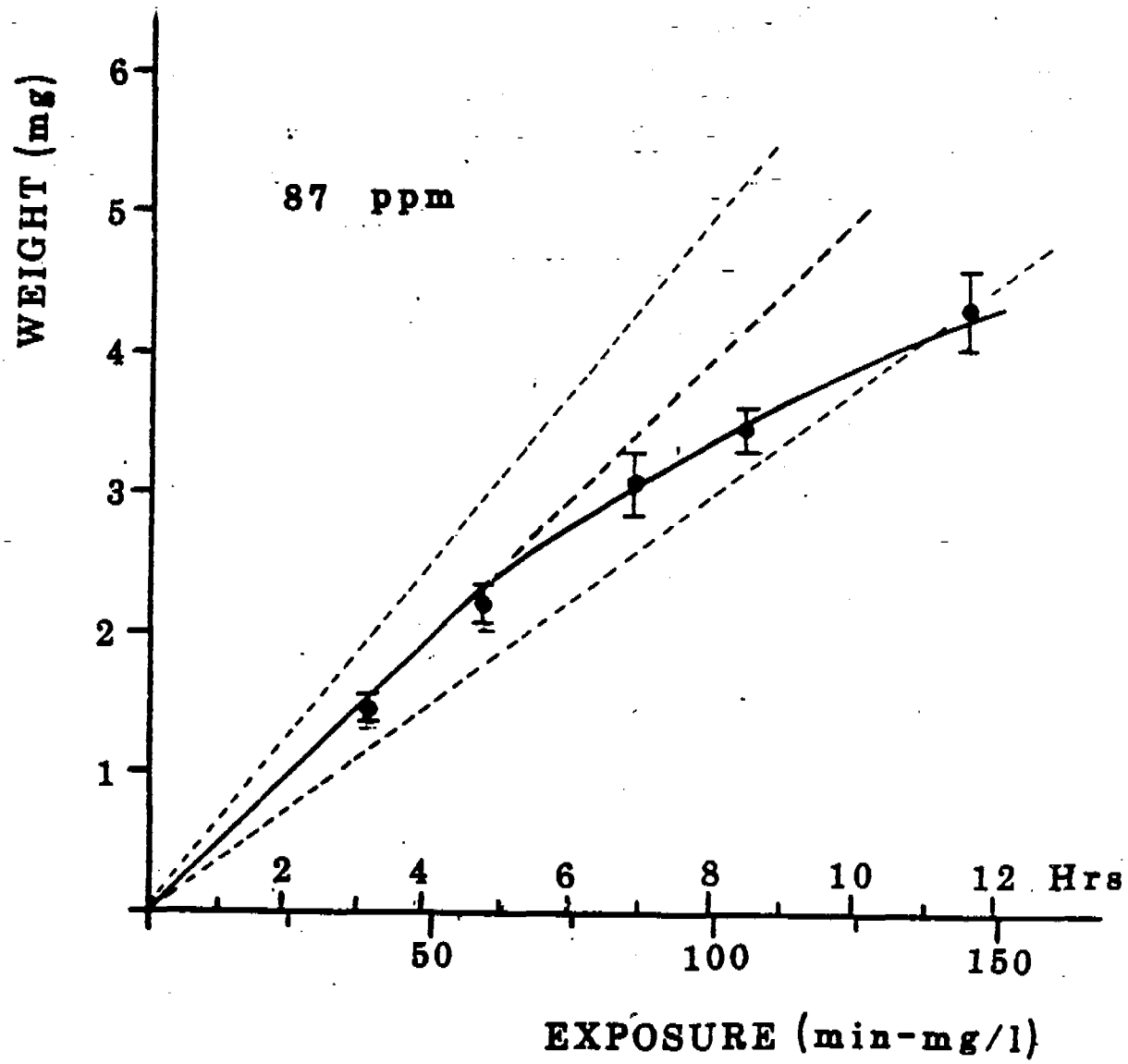
DETERMINATION OF CAPACITY FOR ACETONE





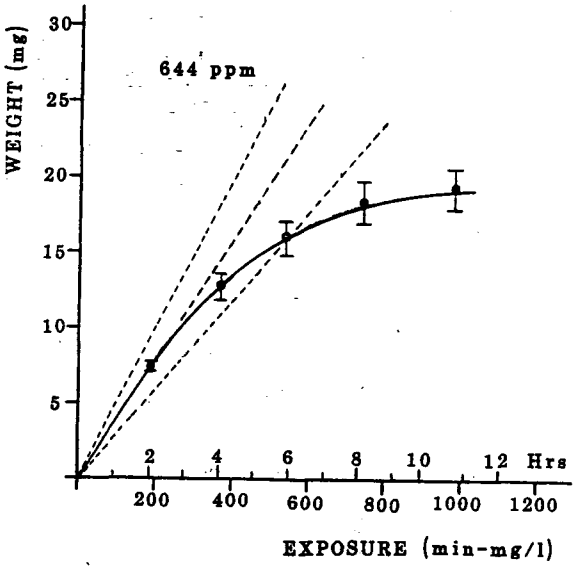
3M 111026

ACETONE



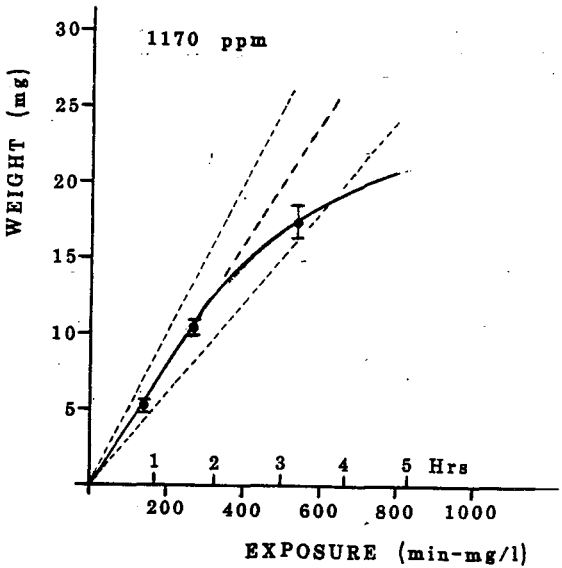
3M 111027

ACETONE



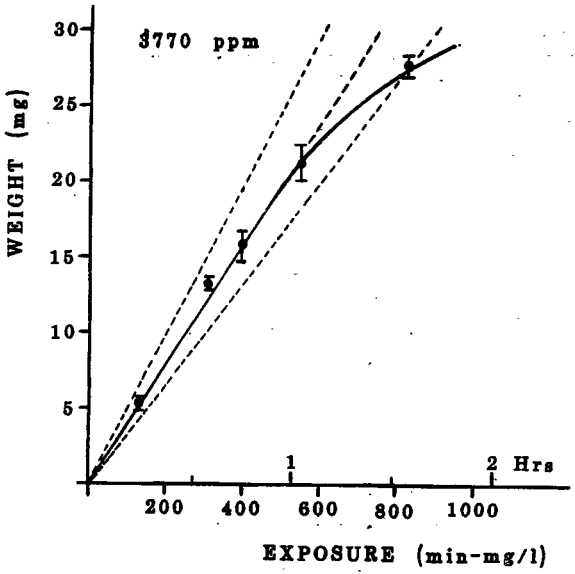
3M 111028

ACETONE



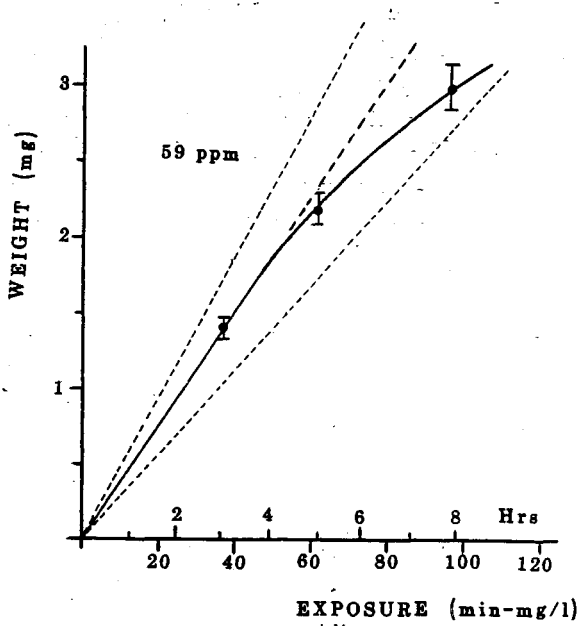
3M 111029

ACETONE

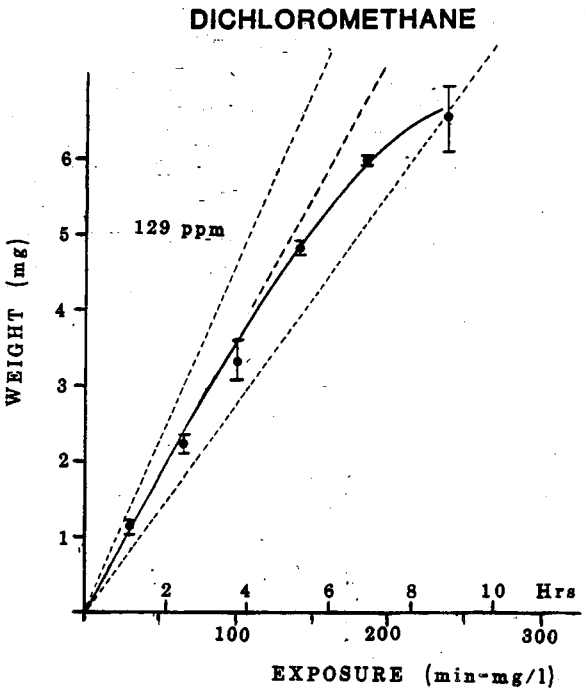


3M 111030

DICHLOROMETHANE

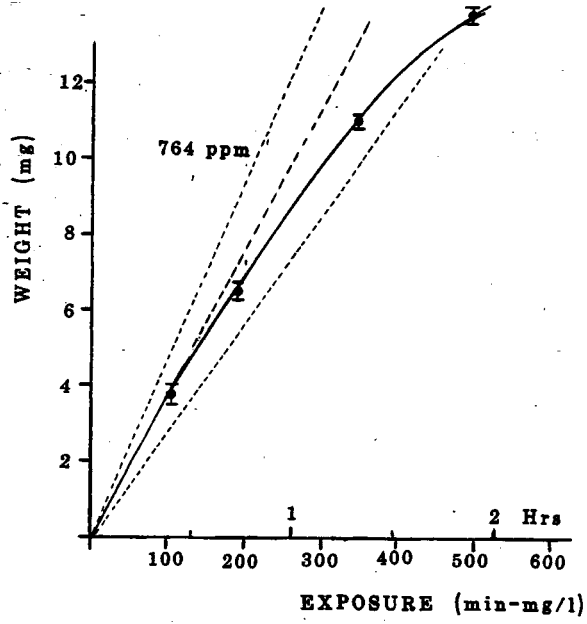


3M 111031


DICHLOROMETHANE
129 ppm
WEIGHT (mg)
1
2
3
4
5
6
2
4
6
8
10
Hrs
100
200
300
EXPOSURE (min-mg/l)

3M 111032

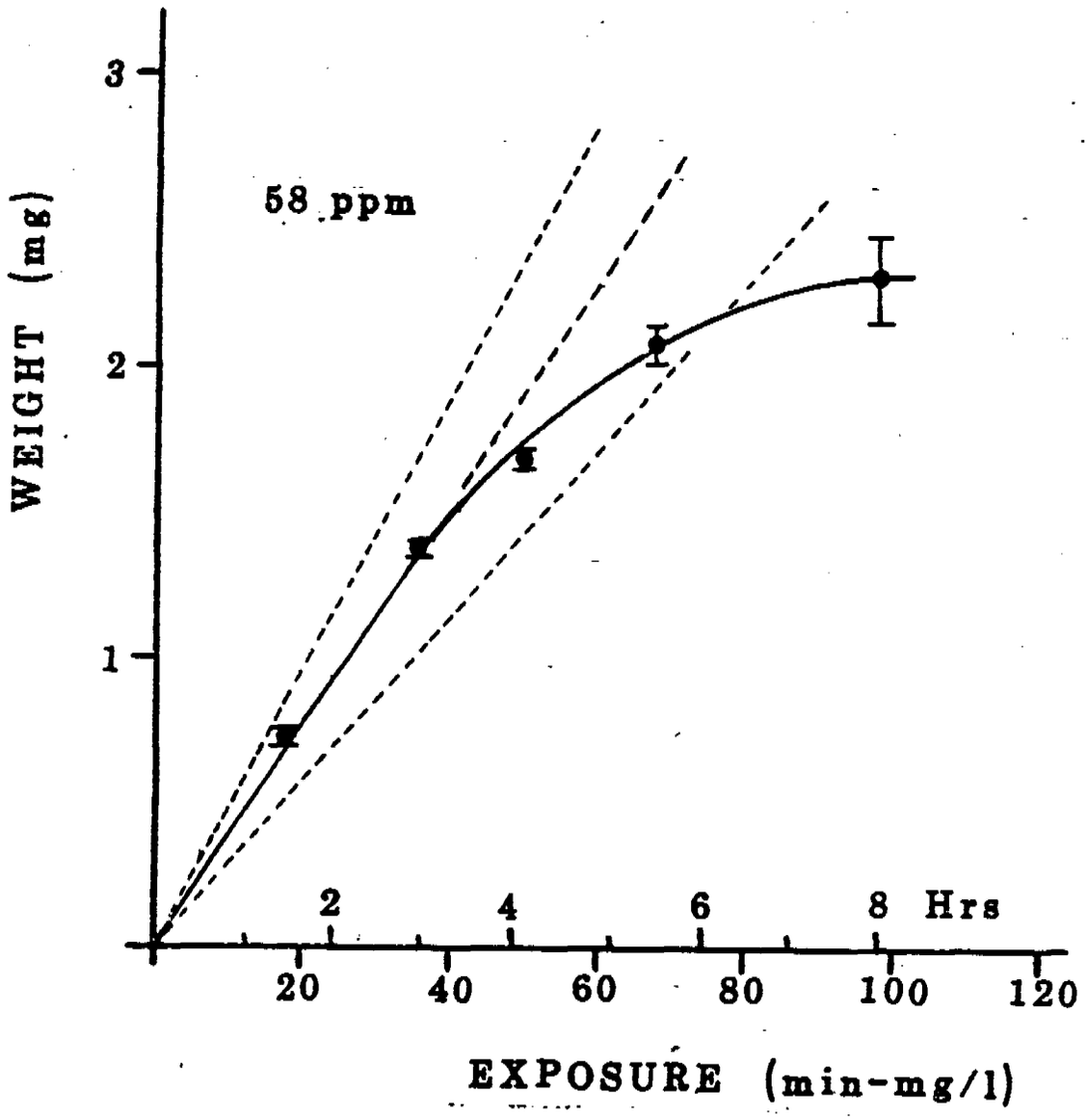
DICHLOROMETHANE



3M 111033

DICHLOROMETHANE

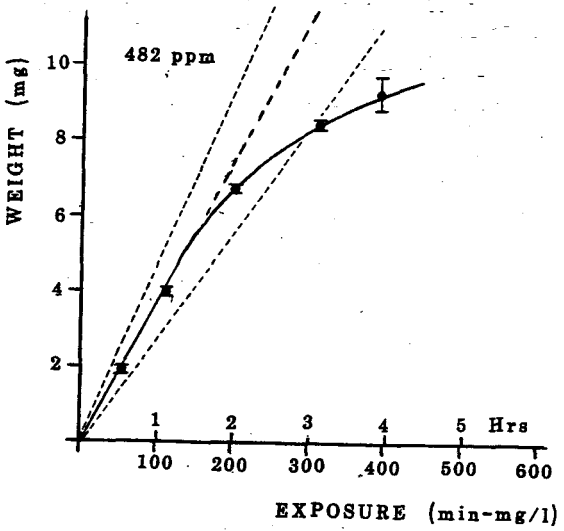
RH - 85%



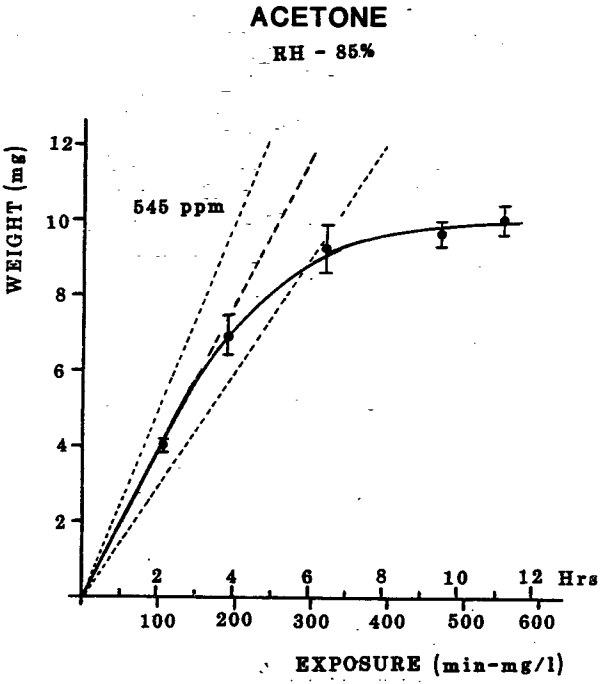
3M 111034

DICHLOROMETHANE

RH - 85%



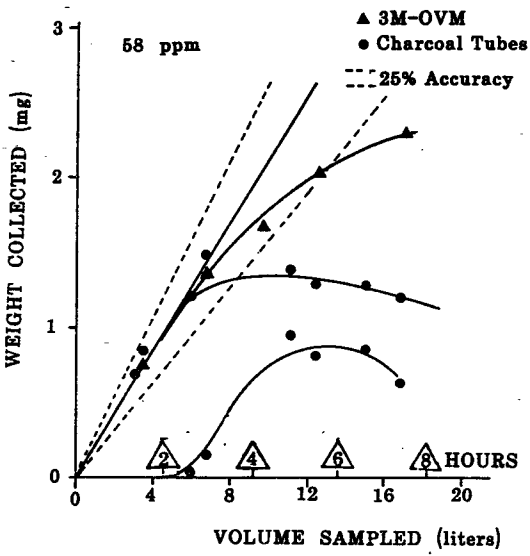
3M 111035


ACETONE
RH - 85%
WEIGHT (mg)
12
10
8
6
4
2
545 ppm
2
4
6
8
10
12 Hrs
100
200
300
400
500
600
EXPOSURE (min-mg/l)

3M 111036

METHYLENE CHLORIDE

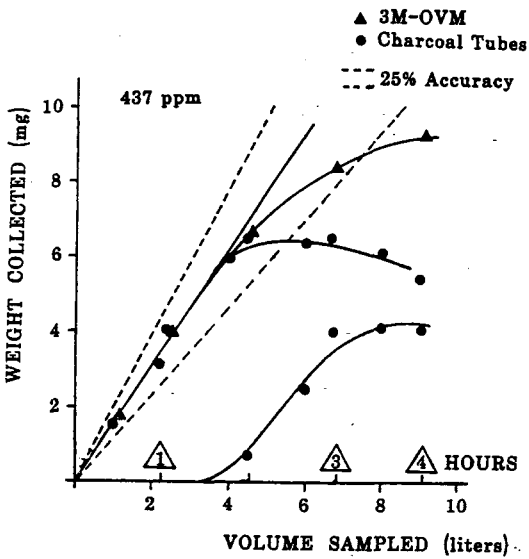
RH-85%



3M 111037

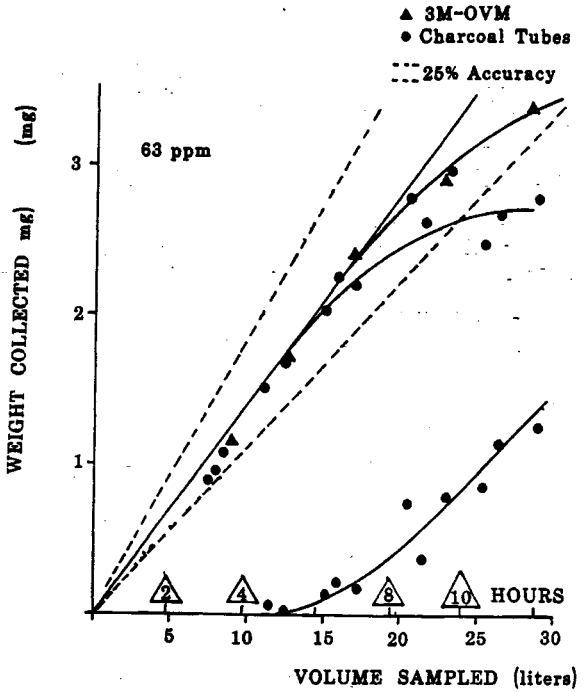
METHYLENE CHLORIDE

RH-85%



ACETONE

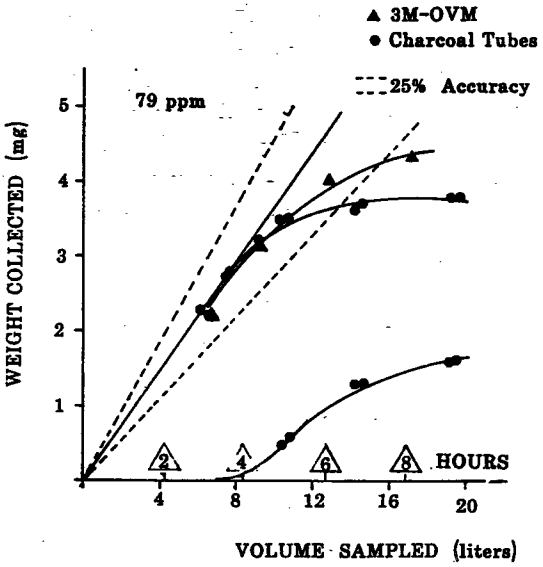
RH-85%



3M 111039

PENTANE

RH-85%



3M 111040

Am. Ind. Hyg. Assoc. J. 46(9):526-531 (1985)

Field Evaluation of Passive Organic Vapor Samplers

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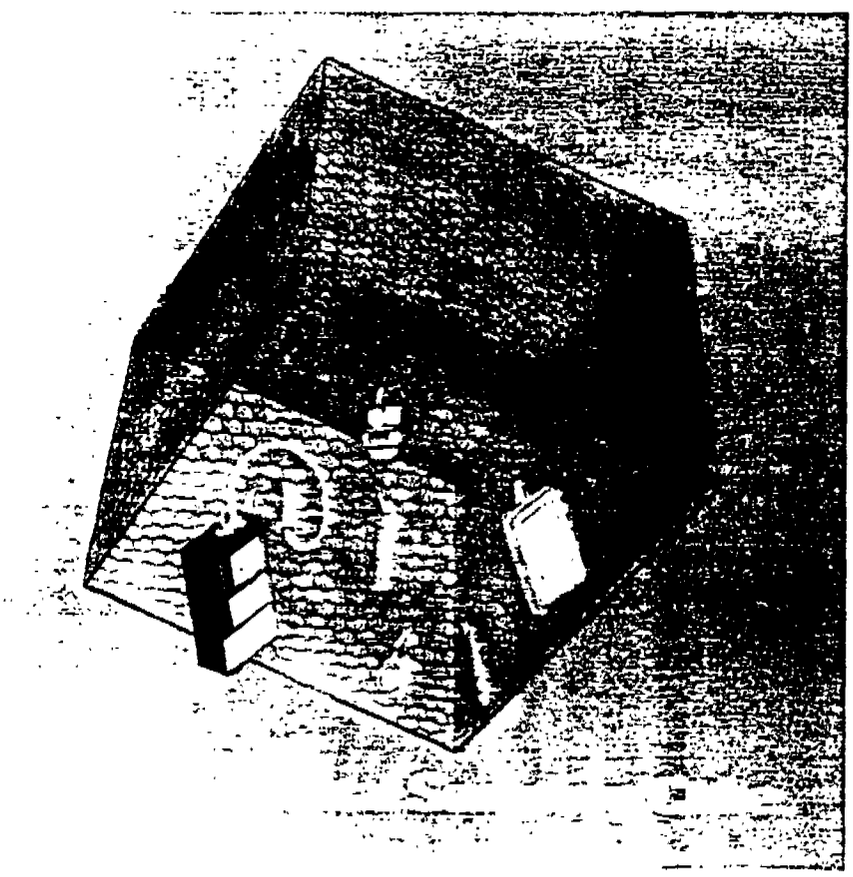
Five diffusion organic vapor monitors and charcoal tubes were exposed to industrial atmospheres containing benzene, toluene and xylene in sets of six a piece in order to evaluate the relative performance of these devices under normal field conditions. The analytical results were treated with two-way analysis of variance, and the least significant difference test was applied to the mean values to further refine the data. The results of this investigation showed that each sampler generally had a high precision. There was, however, a numerically significant difference between the types of samplers. This may be explained by examining the statistics and noting that there was very little variation around the mean values; thus, a small variation between samplers appeared numerically significant. Despite this significant numerical difference, from the pragmatic point of view, the samplers provided essentially equivalent results which allowed the industrial hygienist to determine what action was appropriate. Overall performance of all the sampler types was very good. Each type of sampler could be used for industrial hygiene evaluations with confidence.

Introduction

The passive diffusion-type organic vapor monitor has become much more popular in recent years for use in determining employee exposure to organic vapors. It is easy to use and, as compared to other sampling techniques, requires little attention in the field. Once the diffusion coefficient and badge parameters have been determined, organic vapor concentrations can be simply calculated. Since very little set-up time is required, more employee exposure determinations are possible per survey thus allowing for an expanded surveillance program.

As the accuracy of the charcoal tube method may be affected by sampling pump maintenance and calibration, charcoal tube handling, spontaneous desorption of the organic vapor into the air stream and breakthrough, there are serious questions concerning its accuracy in determining airborne concentrations of organic vapors. In an industrial



3M 111041

Figure 1 — Environmental sampling cube.

TABLE I
Benzene Results
(ppm)
Trial Number 1

Sampling Devices	Repetitions 1	2	3	4	5	6
CT	1.88	1.88	1.68	1.79	2.03	2.07
3M	1.46	1.46	1.43	1.46	1.43	1.46
DP	1.81	1.85	1.73	1.91	1.81	1.81
MSA	1.39	1.39	1.39	1.52	1.44	1.36
ND	1.42	1.68	1.55	1.55	1.42	1.16
NMS	1.69	1.63	1.63	1.77	1.72	1.69

Key: CT — Charcoal Tubes: 3M — 3M Company; DP — DuPont; MSA — Mine Safety Appliances Company; ND — National Draeger; NMS — National Mine Service Company.

Two-Way Analysis of Variance

Grand Mean = 1.62 Grand Range = 1.16-2.07

Level	Col. Mean	Level	Row Mean	Row Std. Dev.
1	1.61	1	1.88	0.15
2	1.65	2	1.45	0.02
3	1.57	3	1.82	0.06
4	1.67	4	1.42	0.06
5	1.64	5	1.46	0.18
6	1.59	6	1.69	0.05

Source	D.F.	Sum of Squares	Mean Square	F-Value
[illegible]	5	1.2464	0.24928	22.858
[illegible]mns	5	0.43922×10^{-1}	0.87844×10^{-2}	0.805
Error.....	25	0.27264	0.10906×10^{-1}	
Total.....	35	1.5630		

(uncontrolled) atmosphere, both the charcoal tube sampling method and the passive diffusion sampling method may be affected by numerous environmental conditions resulting in inaccurate organic vapor determinations. These conditions include air temperature and humidity, multiple air contaminants and air movement.

In reviewing the literature,[1] it is apparent that numerous investigations have centered around comparison of a particular passive organic vapor sampler with charcoal tube evaluations of the same environment under laboratory conditions. In some cases, such laboratory studies were followed by field evaluations. While laboratory conditions are necessary for controlled comparisons, employee exposure monitoring under uncontrolled field conditions is the desired use; thus comparison under the normal environmental conditions encountered by the industrial hygienist provides a pragmatic data set for performance evaluation. Further, a field test of all available organic vapor sampling devices offers a unique comparison opportunity. This comparison of passive diffusion monitors and the charcoal tube sampling method is to determine if the results given by any particular sampling device are statistically equivalent to the corresponding results from all the other devices subject to the same (uncontrolled) industrial environment.

Method

Passive diffusion organic samplers manufactured by five companies and charcoal tubes (SKC, Inc.) were used in this evaluation. The diffusion samplers were manufactured by 3M Company (3M Organic Vapor Monitors®), DuPont (DuPont Pro-tek G-BB Organic Vapor Badges®), Mine Safety Appliances Company (MSA OVD Organic Vapor Dosimeter®), National Mine Service Company (National Mine Service Company Gasbadge®), and National Draeger (National Draeger Orsa 5®). One of each type of sampler plus a charcoal tube were taken to be a set. One set of samplers was placed on each side of an open mesh wire two foot cube (Figure 1). In an industrial atmosphere known to contain vapor phase concentrations of benzene, toluene and xylene, the sampling system was suspended from one corner of the cube, thereby permitting free rotation around a diagonal axis. Free movement of the cube was not restricted in any fashion. Because of the arrangement of the samplers on each face of the sampling cube, each sampler was, at one or more locations on the cube, adjacent to each of the other types of samplers. Thirty-six samplers (six of each type sampler on six faces of the cube) were exposed to essentially the same atmosphere. This sampling procedure was repeated six times in different atmospheres resulting in six replicate sets of data

TABLE II
Benzene Results
(ppm)
Trial Number 2

Sampling Devices	Repetitions 1	2	3	4	5	6
CT	1.72	1.70	1.50	1.38	1.94	1.43
3M	1.23	1.26	1.38	1.38	1.35	1.32
DP	1.63	1.54	1.64	1.67	1.63	1.82
MSA	1.36	1.30	1.33	1.30	1.27	1.27
ND	1.56	1.13	1.56	1.27	0.99	0.99
NMS	1.44	1.51	1.73	1.47	1.60	1.57

Key: CT — Charcoal Tubes: 3M — 3M Company; DP — DuPont; MSA — Mine Safety Appliances Company; ND — National Draeger; NMS — National Mine Service Company.

Two-Way Analysis of Variance

Grand Mean = 1.45 Grand Range = 0.99-1.94

Level	Col. Mean	Level	Row Mean	Row Std. Dev.
1	1.49	1	1.61	0.21
2	1.41	2	1.32	0.06
3	1.52	3	1.66	0.09
4	1.41	4	1.31	0.03
5	1.46	5	1.25	0.26
6	1.40	6	1.55	0.11

Source	D.F.	Sum of Squares	Mean Square	F-Value
Rows	5	0.94056	0.18811	7.658
Columns	5	0.77992×10^{-1}	0.15598×10^{-1}	0.635
Error.....	25	0.61412	0.24565×10^{-1}	
Total.....	35	1.6327		

or thirty-six samples per sampler type with 216 total samples. The air temperature, barometric pressure, relative humidity and air flow rate were recorded at each location during the evaluation. Each sampler was handled in the manner specified by the manufacturer. A sequence of sampler "start times" was followed at the beginning and end of each sample period resulting in essentially the same exposure times for all thirty-six samples on the sampler cube.

All samples were analyzed by carbon disulfide desorption and gas chromatography. Each sample media was placed in a small vial to which the CS_2 was added. Two to five milliliters of CS_2 were used for desorption in order to fully cover the media in the vials. The vials were shaken for 30 min, then analyzed on a Hewlett Packard 5840A Gas Chromatograph with an HP 7672A Automatic Sampler and an HP 5840A GC Terminal. An SP-1000 twenty-foot column at 130° F was used. Injection temperature was 250° F, and the flame ionization detector temperature was 300° F. Evaluation of the automatic injection system indicates duplication of results for a standard solution with standard deviation of 0.05 (10 injection repetitions of standard solution).

Sample results were calculated using manufacturers' instructions for calculations. Desorption efficiency was determined experimentally. Numerous investigators have reviewed desorption of organic compounds from charcoal and reported their results in the literature.[2-9] The diffusion rates necessary for the calculations were supplied by the manufacturer (as diffusion rates or monitor constants).

The data was analyzed using a computer program for two-way analysis of variance. The two hypotheses to be accepted or rejected by this analysis are:

1) Each type of organic vapor sampling device will, when subjected to the same industrial environment, provide a result that is not statistically different from other such devices;

2) Each type of organic vapor sampling device will provide precise measurements of organic vapors in the industrial environment. Such a result will also indicate that the variation of results among each sampler type as a function of being on each side of the cube are not statistically different.

The mean values for each sampling device on each sampling cube were ranked and further evaluated using the least significant difference method of multiple comparisons.

TABLE III
Benzene Results
(ppm)
Trial Number 3

Sampling Devices	Repetitions 1	2	3	4	5	6
CT	1.02	0.95	0.85	0.94	0.91	0.95
3M	0.82	0.73	0.76	0.76	0.79	0.82
DP	1.13	0.84	1.48	2.05	1.92	1.83
MSA	0.83	0.74	0.86	0.71	0.86	0.86
ND	0.85	0.85	0.99	0.85	0.99	0.99
NMS	1.13	1.04	1.10	0.94	1.00	1.16

Key: CT — Charcoal Tubes; 3M — 3M Company; DP — DuPont; MSA — Mine Safety Appliances Company; ND — National Draeger; NMS — National Mine Service Company.

Two-Way Analysis of Variance

Grand Mean = 1.01 Grand Range = 0.71-2.05

Level	Col. Mean	Level	Row Mean	Row Std. Dev.
1	0.96	1	0.94	0.06
2	0.86	2	0.78	0.04
3	1.01	3	1.54	0.48
4	1.04	4	0.81	0.07
5	1.08	5	0.92	0.08
6	1.10	6	1.06	0.08

Source	D.F.	Sum of Squares	Mean Square	F-Value
Rows	5	2.3502	0.47004	11.476
Columns	5	0.23550	0.47100×10^{1}	1.150
Error.....	25	1.0240	0.40960×10^{1}	
Total.....	35	3.6097		

TABLE IV
Benzen Results
(ppm)
Trial Number 4

Sampling Devices	Repetitions 1	2	3	4	5	6
CT	4.67	3.56	4.03	3.97	3.56	4.41
3M	3.12	3.01	3.09	3.04	3.04	3.01
DP	4.33	4.30	4.91	4.44	4.52	4.66
MSA	2.50	2.39	2.60	2.57	2.32	2.78
ND	2.79	2.85	2.85	2.97	3.33	2.62
NMS	4.01	4.01	4.01	3.85	3.72	3.80

Key: CT — Charcoal Tubes; 3M — 3M Company; DP — DuPont; MSA — Mine Safety Appliances Company; ND — National Draeger; NMS — National Mine Service Company.

Two-Way Analysis of Variance

Grand Mean = 3.49 Grand Range = 2.39-4.91

Level	Col. Mean	Level	Row Mean	Row Std. Dev.
1	3.57	1	4.03	0.45
2	3.35	2	3.05	0.04
3	3.58	3	4.53	0.23
4	3.47	4	2.53	0.16
5	3.42	5	2.90	0.23
6	3.55	6	3.90	0.13

Source	D.F.	Sum of Squares	Mean Square	F-Value
Rows	5	18.026	3.6051	59.451
Columns	5	0.25557	0.51113×10^{1}	0.843
Error.....	25	1.5160	0.60640×10^{1}	
Total.....	35	19.797		

TABLE V
Benzene Results
(ppm)
Trial Number 5

Sampling Devices	Repetitions 1	2	3	4	5	6
CT	3.60	3.49	3.41	3.60	3.22	4.25
3M	3.10	3.03	3.13	3.28	3.18	3.05
DP	4.72	4.42	4.55	4.77	5.41	4.46
MSA	2.39	2.48	2.51	2.68	2.78	2.58
ND	3.12	3.12	2.08	2.42	3.00	2.77
NMS	3.82	3.74	4.18	4.10	3.92	4.07

Key: CT — Charcoal Tubes; 3M — 3M Company; DP — DuPont; MSA — Mine Safety Appliances Company; ND — National Draeger; NMS — National Mine Service Company.

Two-Way Analysis of Variance

Grand Mean = 3.46 Grand Range = 2.08-5.41

Level	Col. Mean	Level	Row Mean	Row Std. Dev.
1	3.46	1	3.60	0.35
2	3.38	2	3.13	0.09
3	3.31	3	4.72	0.24
4	3.48	4	2.57	0.14
5	3.59	5	2.75	0.42
6	3.53	6	3.97	0.17

Source	D.F.	Sum of Squares	Mean Square	F-Value
Rows	5	19.654	3.9307	45.313
Columns	5	0.29745	0.59489×10^{-1}	0.686
Error.....	25	2.1666	0.86745×10^{-1}	
Total.....	35	22.120		

Discussion

In 1970 White, *et al.*[10] suggested that solvent vapors in the industrial atmosphere could be measured using charcoal tubes. This procedure was reviewed numerous times in the literature and ultimately accepted by the National Institute for Occupational Safety and Health (NIOSH) as the recommended practice. This method for organic vapor sampling uses a low-flow sampling pump and an activated charcoal sampling tube. The charcoal tube is a glass tube containing two sections of 20/40 mesh activated charcoal with appropriate partitions. The front section of the tube usually contains 100 mg of activated charcoal, and the back-up section, used for evaluation of breakthrough (saturation of the front section) and/or migration of the sample, usually contains 50 mg of activated charcoal. The sampling pump flow rate is calibrated to approximately 100 cubic centimeters per minute for optimum collection of many organic vapors.

In the mid-1970s, the use of diffusion monitors for organic vapor analysis became a viable approach to the evaluation of employee exposures to such vapors. Although these devices are available in a variety of shapes and sizes, each uses the same basic approach to the collection of organic vapors. The use of such "badges" has been hailed as great progress in simplifying the evaluation of employee exposures as these devices do not need individual flow calibrations, maintenance or batteries essential to charcoal tube sampling.

The benzene analysis results of this investigative comparison are shown in Tables I through VI. For each table of results, each device on each side of the sampling cube (noted as repetitions) was exposed to essentially the same atmosphere; thus, the results should be the same. Ideally, if all the samplers were identical, all the thirty-six sample results in each table would be the same result. The analysis of variance for each result on each sampling cube is noted below the corresponding table of results. The statistic for comparison is the calculated F value based on an $\alpha = 0.05$ level which is $F_{(0.05,5,25)} = 2.60$.

The analysis of variance for all the benzene results tables shows the column's F-value is less than the statistic; thus, each type of sampling device provided results which did not exhibit a statistically significant difference for the repetitions of that device within each test. The hypothesis that each type of sampling device is precise is therefore accepted. This result also serves to validate the use of the sampling cube as a device for multiple samples within an environment as a method for comparisons through simultaneous sampling repetition. This use of the sampling cube did not interfere with producing statistically similar responses from the sam-

TABLE VI
Benzene Results
(ppm)
Trial Number 6

Sampling Devices	Repetitions 1	2	3	4	5	6
CT	5.04	4.86	5.01	4.67	5.84	5.13
3M	4.19	3.92	4.17	4.78	4.12	4.07
DP	6.08	4.57	6.29	4.70	6.14	6.37
MSA	3.34	3.19	3.39	3.68	3.46	3.80
ND	3.96	3.51	3.62	3.85	3.85	3.96
NMS	5.32	4.97	5.67	5.45	5.10	5.30

Key: CT — Charcoal Tubes; 3M — 3M Company; DP — DuPont; MSA — Mine Safety Appliances Company; ND — National Draeger; NMS — National Mine Service Company.

Two-Way Analysis of Variance

Grand Mean = 4.62 Grand Range = 3.19-6.37

Level	Col. Mean	Level	Row Mean	Row Std. Dev.
1	4.82	1	5.27	0.56
2	4.17	2	4.21	0.30
3	4.69	3	5.69	0.90
4	4.52	4	3.48	0.23
5	4.75	5	3.79	0.19
6	4.78	6	5.30	0.25

Source	D.F.	Sum of Squares	Mean Square	F-Value
Rows	5	25.165	5.0329	29.247
Columns	5	1.8052	0.36104	2.098
Error.....	25	4.3020	0.17208	
Total.....	35	31.272		

TABLE VII
Rank of Mean Values
(ppm)

Benzene Rank	Test No. 1	2	3	4	5	6
1	CT 1.58	DP 1.66	DP 1.54	DP 4.53	DP 4.72	DP 5.69
2	DP 1.82	CT 1.61	NMS 1.06	CT 4.03	NMS 3.97	NMS 5.30
3	NMS 1.69	NMS 1.55	CT 0.94	NMS 3.90	CT 3.60	CT 5.27
4	ND 1.46	3M 1.32	ND 0.92	3M 3.05	3M 3.13	3M 4.21
5	3M 1.45	MSA 1.31	MSA 0.81	ND 2.93	ND 2.75	ND 3.79
6	MSA 1.42	ND 1.25	3M 0.78	MSA 2.53	MSA 2.57	MSA 3.48
LSD =	0.12	0.18	0.24	0.29	0.35	0.49

Key: CT — Charcoal Tubes; 3M — 3M Company; DP — DuPont; MSA — Mine Safety Appliances Company; ND — National Draeger; NMS — National Mine Service Company.

pling devices on various sides of the cube, either as a result of the sampling space size or as an obstruction or interferent in the sampling process.

The analysis of variance evaluation for each of the Tables I through VI also shows the row mean values and the row standard deviation. These calculations and the mean square error values illustrate the generally very small variation around the mean values for each sampling device in each test. Thus, a small variation between the mean value results for each type of sampling device is likely to be statistically significant. Such a significant difference is evidenced by the generally large F values for the rows as listed in each analysis of variance. When subjected to the same industrial environment, the hypothesis that each type of organic vapor sampling device will provide a result that is not statistically different from other such devices is therefore rejected. Each type of sampling device tested will produce a statistically different result as compared to the other devices when exposed to the same industrial environment.

Armitage[11] states "It will usually be important not to rely solely on the analysis of variance table and its F test, but to examine the difference between groups more closely to see what patterns emerge". The method recommended for further analysis is calculation of the Least Significant Difference (LSD). This is shown in Table VII for the LSD at the 5% level for the sampling devices' results in all six tests. With the LSD test, it is clear where the differences between the mean values for each test result is significant. The values in Table VII indicate inconsistency in the ranked mean value for each type of sampling device; that is, for some benzene tests, the sampling devices rank in a particular order, while in other benzene tests, they rank in a completely different order.

The current NIOSH standard method for evaluation of organic vapor concentrations is the use of charcoal tubes. If we concede this to be the "standard", then further analysis of the data in Table VII can be accomplished by adding and subtracting the LSD value from the charcoal tube mean value for each test. This procedure is illustrated in Table VII with solid lines bracketing the sampling device results which are within ±LSD of the charcoal tube mean value. If inclusion within the bracket is termed agreement (accuracy), then for the benzene analysis, the National Mine Service monitor is in agreement with the charcoal tube result 67% of the time, the DuPont monitor is in agreement 50% of the time, and the other monitors are in agreement less than 50% of the time. As previously noted, this investigation involved sampling device analysis for benzene, toluene and xylene. All the data can be subjected to the same statistical treatment as was the benzene data with the result presented in Table VIII. Overall, the 3M monitor is in agreement with the charcoal tube result 50% of the time, the DuPont and Mine Safety Appliances monitors agree with the charcoal tube result 39% of the time, and the National Draeger and National Mine Service monitors agree with the charcoal tube result 33% of the time.

A pragmatic approach to the data is to evaluate the average results of each sampling method with respect to criteria used for industrial hygiene occupational exposures. The current Occupational Safety and Health Administration Permissible Exposure Limits (PEL) for exposures to benzene, toluene and xylene are 10 ppm, 200 ppm and 100 ppm

TABLE VIII
Passive Organic Vapor Samplers' Results
Agreement with Charcoal Tube Results

Sampler	% Agreement* Benzene	Toluene	Xylene	Overall
3M	17	67	67	50
DP	50	67	0	39
MSA	17	0	100	39
ND	17	17	50	33
NMS	67	0	33	33

*Percent of the sampling device results which are within plus or minus the Least Significant Difference (±LDS) of the Charcoal Tube result for the same test.

Key: 3M — 3M Company; DP — DuPont; MSA — Mine Safety Appliance Company; ND — National Draeger; NMS — National Mine Service Company.

respectively. In each benzene, toluene and xylene test, the average results illustrate a relationship between an atmospheric concentration of the contaminant and the OSHA PEL. The industrial hygienist must evaluate the results of the sample with respect to the operation involved and related medical information to determine the extent of any potential health hazards. Using a sampling system that gives results which may vary from those given by another sampling system by 20% or 2 ppm for benzene, or by 40 ppm and 20 ppm for toluene or xylene, respectively, should not significantly change the action to be taken by the industrial hygienist. If any sampling system indicates organic vapor concentrations in PEL ranges even with 20% variation in results, additional action is essential. Sampling results must be combined with operations data, medical data and other significant data to determine the course of action to be taken. Consistent and repetitious air monitoring should indicate patterns which can be used to protect the health of the employees. For a more specific relationship between charcoal tubes and a particular diffusion organic vapor sampler, tests should be conducted with the organic compound of interest under conditions most like the actual sampling conditions to be encountered. In summary, the major source of variability is between types of samplers: therefore, the greatest reduction of variability would be achieved by consistent use of one sampler type.

Acknowledgements

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A two-phase study was conducted to assess the suitability of passive monitoring for the collection of airborne vapor degreasing solvents under laboratory and field conditions. The laboratory stage of the investigation involved the determination of collection efficiencies for methyl chloroform (MC) and trichloroethylene (TCE). A 6920 L static chamber was used to establish standard atmospheres of these solvents at various concentrations, which were then sampled using passive monitors; samples were subsequently analyzed by gas-liquid chromatography. In the second part of the investigation, several MC and TCE vapor degreaser operations were monitored at US Army industrial plants. The purpose of the field study was to develop worker exposure profiles and to obtain a side-by-side comparison of the passive monitor with the traditional charcoal tube sampler. Presented are statistically reduced data and the performance characteristics of both collection techniques.

Evaluation of passive monitors for assessing vapor degreaser emissions

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Introduction

Vapor degreasing is one of the most widely used of all metal cleaning techniques. It is suitable for cleaning all common industrial metals without the danger of etching or chemical attack. Furthermore, the process is relatively economical, and it is adaptable to parts in a wide range of sizes and shapes. This operation is used extensively by the metal fabrication industry to remove soils before applying protective coatings, electroplating, and before and after machining. Metal cleaning varies in quantity and complexity from small manual operations in which parts or tools are cleaned by solvent-dipping to mass production degreasing where large volumes of metal parts are cleaned in units of great capacity having sophisticated engineering controls. Solvents most commonly used are methyl chloroform (1,1,1-trichloroethane), trichloroethylene, perchloroethylene, methylene chloride, and trichlorotrifluoroethane. Of these, methyl chloroform (MC), and trichloroethane (TCE) are the most prominent.

A solvent vapor degreaser consists of a tank or vat with a heat source in the lower section to vaporize the solvent and a cool area in the upper section to condense the vapor. The parts to be cleaned are suspended in the vapor zone between the hot solvent and cool area. As the solvent condenses and flows over the cool parts, it removes greases, oils, and other soils, and returns to the hot solvent. When the parts reach the temperature of the vapor, condensation stops and the parts become dry.

The Army operates numerous vapor degreasers of various sizes at installations throughout the country. The majority of these units were originally designed for use with TCE, however, almost all have been converted to methyl chloroform systems. If conducted properly, vapor degreasing operations are safe and efficient. On the other hand, when standard operating procedures are not strictly observed or when obsolete or faulty equipment is used, solvent losses may occur which could easily cause worker exposures to reach hazardous levels.

NIOSH has estimated that workers exposed to MC and TCE in the United States alone number approximately 200 000 and 100 000 respectively.[1,2] The most common industrial use of these solvents is as degreasing agents. The present US Federal standard for an 8-hour time-weighted average exposure to MC is 350 ppm. The recommended standard takes into account central nervous system responses to acute exposures in man,[3-5] respiratory and cardiovascular effects in several animal species associated with chronic exposures,[6,7] and the absence of reported effects in man at concentrations below the recommended standard.

The US Federal recommended standard for an 8-hour time-weighted average exposure to TCE is currently 100 ppm; for 15 minute exposures, 150 ppm may not be exceeded. This TCE standard is supported by studies showing the slight psychophysiological effects observed at 100 ppm,[8] respiratory and prenarcosis effects at concentrations between 200 and 500 ppm,[9-11] and subject responses at 150-200 ppm.[9,10] Fatalities have been reported[12,13] when workers were exposed to levels estimated to be between 1700 and 3300 ppm for 10 minutes.

The NIOSH criteria documents for MC and TCE specify the charcoal tube method for the collection of breathing zone samples.[1,2] This time-tested technique is capable of providing accurate and reliable results; however, it does not offer the convenience, compactness, and nonmechanical reliability of diffusion type passive monitors. Since the advent of the organic vapor passive monitor (OVPM), sev-

The opinions or assertions contained herein are the private views of the authors and are not to be construed as reflecting the views of the Department of the Army or the Department of Defense.

Use of trademarked names does not imply endorsement by the US Army, but is used only to assist in identification of a specific product.

eral controlled laboratory studies on the performance of these devices have been reported.[14-16] In addition, Boeniger *et al.*[17] conducted a field comparison of two diffusion passive monitors with charcoal tubes under singular and multiple exposure conditions. Our laboratory has conducted laboratory and field studies[3,19] to assess their applicability to various industrial hygiene related problems. None of the forementioned studies have dealt with the collection and analysis of MC and TCE in both field and controlled environments.

This report presents the results of field and laboratory comparisons of the DuPont Pro-Tek (DPT) and 3M Organic Vapor Monitor (OVM) diffusion passive monitors with the charcoal tube for collecting MC and TCE. The laboratory study consisted of the determination of collection efficiency, desorption efficiency, and storage stability of each device. Performance characteristics in the field were determined at several locations where MC and TCE were being used routinely. Two of these sites were selected because of previously reported high concentrations of vapors in the areas around the degreasing tanks. Both personal and stationary samples were collected; some monitors were intentionally subjected to high exposures for long periods of time in order to ascertain the capacity of the OVPM's. Comparative data for all three samplers are presented.

experimental

air sampling equipment

Passive monitoring was conducted with the 3500 Organic Vapor Monitor®, 3M Company, St. Paul, MN, and the Pro-Tek® Organic Vapor Badge, E.I. DuPont de Nemours & Co. (Inc.), Wilmington, DE.

Both devices consist of an inert plastic body, diffuser, and charcoal collection element. Contaminants enter the monitor via molecular diffusion, traverse the air space between the monitor face and collection element, and are adsorbed on the charcoal collection pad. After sampling is terminated, the monitor is covered and then sealed in an aluminum foil bag provided by the manufacturer. The mass of the material collected on the charcoal is determined by gas chromatography (GC) subsequent to desorption with carbon disulfide.

Both the OVM and DPT have design characteristics which offer distinct and unique advantages over each other. For example, the OVM is constructed so that the desorbing solvent can be added directly to the monitor body. Other monitors require that the charcoal collection element be transferred to a desorption vial prior to treatment with carbon disulfide. Additionally, most passive monitors have a fixed sampling rate which is predetermined by the diffusion coefficient of the analyte and geometry of the monitor. The DPT, however, provides the capability of sampling at two different rates depending on whether one or both of its covers are removed during exposure. All the work described in this paper was conducted with only one of the covers removed. MC and TCE sampling rates provided by the manufacturers are 28.0 cc/min for both MC and TCE for the 3M OVM, 30.2 cc/min MC and 32.6 cc/min TCE for the DuPont Pro-Tek (single cover sampling).

The time-weighted worker exposure is calculated using the following equations:

$$mg/m^3 = \frac{\text{corrected weight on badge (nanograms)}}{\text{sampling rate (cm}^3\text{ min)} \times \text{sampling time (min)}}$$

$$ppm = \frac{mg}{m^3} \times \frac{22.4\text{ L mole}}{\text{mwg/ mole}} \times \frac{T\,^\circ K}{273\,^\circ K} \times \frac{760\text{-mm Hg}}{P\text{-mm Hg}}$$

Charcoal tube collection was conducted with tubes (200, 400 mg) purchased from SKC Inc., Eighty Four, PA. Samples were collected at a nominal rate of 0.050 L min using Accuhaler 808 pumps (MDA, Park Ridge, IL) which were calibrated before and after field usage. Air sample volumes were determined by multiplying the air volume per stroke (determined in the laboratory) by the number of strokes indicated on the counter.

gas chromatography

The charcoal tubes and monitors were all analyzed using the same technique, *i.e.*, one and one-half mLs of carbon disulfide were added to the charcoal, samples were shaken with the CS_2, and allowed to desorb for 30 minutes. Analyses of carbon disulfide desorbent solutions were performed on a Hewlett-Packard Model 5830 gas chromatograph equipped with a flame ionization detector and HP 18850A GC Terminal. The GC operating conditions were as follows: column, 10 ft × 1/8 inch stainless steel packed with 10 percent FFAP on 80-100 mesh Chromosorb W-HP; injection port temperature, 250 °C; detector temperature, 250 °C; column temperature, 110 °C.

laboratory testing

Appropriate amounts of MC or TCE were introduced into a 2-mL vial and sealed with a screw cap. The vial was trans-

TABLE I
Methyl Chloroform Field Data

Loading Range ppm-hrs	Samples No.	OVM Mean Recovery %	Rel Std Dev %	DPT Mean Recovery %	Rel Std Dev %
21 - 65	4	107.6	5.4	115.6	9.1
115 - 200	7	114.9	3.5	115.3	6.7
211 - 285	4	99.6	6.8	103.5	4.3
410 - 532	3	95.6	12.0	91.0	6.3
Overall	18	106.7	9.8	108.7	11.4

TABLE II
Trichloroethylene Field Data

Loading Range ppm-hrs	Samples N	OVM Mean Recovery %	OVM Std Dev %	DPT Mean Recovery %	DPT Std Dev %
11 - 141	15	110.5	21.8	108.1	12.0
207 - 300	5	108.6	21 0	90.7	15.0
359 - 842	5	100.4	6.6	94 7	5.2
1161 - 2090	3	91.8	7 6	89 0	9.1
3249 - 11 116	3	89.0	18.5	74.5	26.0
Overall	31	103.4	19.0	97.4	16.7

ferred to a 6920 liter static test chamber and positioned in front of a circulating fan. The vial cap was removed and the chamber door closed immediately. After sealing the door, the circulating fan was run for 30 minutes to vaporize the test sample and allow the chamber concentration to equilibrate. The circulating fan remained on throughout the entire testing period. The monitors were attached to a meter stick and introduced into the test atmosphere through a side access port of the chamber. CT samples were collected at a port adjacent to the passive monitors. Two or three successive CT samples were collected during each of the passive monitor exposures. Samples were generally analyzed within 24 hours after collection.

comparative field sampling

An attempt was made to locate each sampler of a set in the ame environment without compromising the integrity of ny other sampler. Obviously, some variance in contaminant concentration is to be expected in the field even when samplers are in close proximity with each other. Most of the stationary sampling was performed by positioning 3 CT's, 2 OVM's, and 2 DPT's side-by-side in an alternating pattern 2 inches apart starting with a CT. To study possible "starvation" effects induced by competitive sampling of monitors, some tests were conducted by randomly spacing 2 or 3 samplers 6 inches from adjacent samplers.

Personal samples were collected by attaching a CT, DPT, and OVM to the collar or lapel of the worker being monitored. All of the survey samples were kept at room temperature prior to chromatographic analysis which was performed 1-3 weeks after sample collection.

desorption efficiency

Desorption efficiencies for MC and TCE were determined using the phase equilibrium technique. Known concentrations of MC and TCE were prepared in carbon disulfide and aliquots were added to each of the monitors. The carbon disulfide solutions were allowed to interact with the carbon for 30 minutes with occasional mixing. Desorption efficiencies were determined by comparing the GC analyses of standards before and after addition to the monitors.

sults and discussion

The first phase of the test program was to determine the efficiency of the passive monitors under controlled laboratory conditions. All tests were conducted at room temperature in the 6920 liter chamber previously described: theoretical concentrations covered the ranges of approximately 1/2 - 2 TLV for MC and 1/5 - 2 TLV for TCE. This study was initiated before the DPT badges became commercially available; consequently, fewer DPT badges were included in the laboratory phase of the investigation. Based on the analysis of 20 OVM badges and 6 DPT badges exposed to methyl chloroform, the coefficient of variation in the 160 - 840 ppm range was 0.045 for DPT and 0.047 for OVM. These values correspond to a relative standard deviation of 15.7 and 16.5 ppm for DPT and OVM, respectively at 350 ppm (TLV for MC). In the trichloroethylene chamber study, 27 OVM and 10 DPT badges were exposed to concentrations of TCE in the range of 20 - 200 ppm. The coefficient of variation in this range was 0.076 and 0.07" for the OVM and DPT, respectively. These values correspond to a relative standard deviation of 7.6 ppm for the OVM and 7.7 ppm for the DPT at 100 ppm (TLV for TCE). Based on the chamber study the mean percent recovery for methyl chloroform was found to be 93.8, 89.1, and 95.1 for the OVM, DPT, and CT, respectively. For TCE the mean percent recovery equalled 96.3 for OVM, 93.6 for the DPT, and 95.4 for the CT. Since the purpose of the laboratory study was to determine empirical factors for correcting field survey samples, the given values were not corrected for desorption efficiencies which were found to be between 96 and 100 percent for all three devices.

Tables I and II show the data of all the samples collected in the field and comprise both personal and stationary samples. These data are arranged in order of increasing sampler loading expressed as ppm-hours. The loading ranges were calcu-

TABLE III
Statistical Data - Field Samples

Sample, Comparison	Slope	Correlation Coefficient
TCE Personal (CT/OVM)	1 08	0.98
(CT/DPT)	1.00	0.98
TCE Stationary (CT/OVM)	1.06	0.98
(CT/DPT)	0.99	0.98
MC Personal (CT/OVM)	1.07	0.98
(CT/DPT)	0.99	0.94
MC Stationary (CT/OVM)	0.90	0.89
(CT/DPT)	0.98	0 94

TABLE IV
Storage Stability

Storage Time (Weeks)	OVM Concentration (ppm) Within 24-Hours	OVM Concentration (ppm) After Storage Time	DPT Concentration (ppm) Within 24-Hours	DPT Concentration (ppm) After Storage Time
METHYL CHLOROFORM				
2	45.2	45.6	253	249
2	285.0	299 0		
3	45.2	44.3	253	243
3	285 0	284 0		
TRICHLOROETHYLENE				
2	85.9	89 3	82.0	82.0
3			82.0	84 2

lated by multiplying the ppm concentration found on the CT times the hours sampled. For interpretive purposes, the OVM and DPT field results are reported relative to the CT results. All field results were corrected using the mean percent recoveries determined in the laboratory. Stationary sample results were obtained in each case by comparing the average of two (each type) passive monitors with the average concentration from three CT's.

Field data for MC, Table I, includes 11 personal and 7 stationary samples. Samples were collected over time periods extending 1 - 5 hours, at temperatures between 60 and 70 ° F and relative humidities of 35 and 45 percent. As can be seen in Taole I, lower badge loadings resulted in higher recoveries. However, over the range tested, the overall mean recoveries for both monitors were in good agreement with the charcoal tubes results and with each other.

TCE field data are presented in Table II. At the area monitored, the temperatures ranged from 65 - 75 ° F; relative humidity remained around 30 percent. As shown in this Table, the relative mean recovery for the OVM and DPT passive monitors was 103.4 and 97.4 percent, respectively. In some tests, badges were intentionally held at high TCE concentrations for long periods of time to promote high badge loadings (3249 - 11 116 ppm-hours). To preclude the overloading of charcoal tubes that were run concurrently with the badges, a series of three charcoal tubes were run consecutively with each badge exposure. As shown in Table II, good passive monitor recoveries were obtained with exposures up to 2040 ppm-hours; at the 3249 - 11 116 range, recoveries decreased significantly, an indication of overloading. These results are in agreement with the manufacturers' upper exposure limits recommended for TCE. With the exception of the overloaded monitors, good correlations were obtained between the passive monitors and charcoal tubes. It can also be noted that the recovery of TCE followed the same pattern as the case of MC; at the lower loadings higher recoveries were obtained; conversely, recoveries decreased as the badge loadings increased.

This effect has been predicted by J. Martin from theoretical treatments of sorption phenomena and has been observed in experimental data. It is believed to be the result of a gradual decrease in available active sites for sorption, forcing the organic molecules to move farther into the sorbent in order to be bound.[20]

Table III presents the calculated slopes of regression lines and correlation coefficients of paired sample results for comparisons of CT and passive dosimeter field data. As indicated, the slopes and correlation coefficients are very close to unity.

The results of storage stability tests are presented in Table IV for the OVM and DPT. The monitors were exposed in the static chamber to MC and TCE, sealed in aluminum foil bags, and stored for up to 3 weeks at room temperature. As shown, no significant losses occurred when OVM's and DPT's containing MC and TCE were stored for periods as long as three weeks.

As discussed above, passive monitor recoveries for field samples were calculated from results of charcoal tubes samples concurrently. In essence, the CT results were taken as the "true value" of the concentration present. It must be recognized that such comparisons can be somewhat misleading. Sampling errors of 7% and more have been documented for collecting TCE with CT's under controlled laboratory conditions.[21] Errors may be due to such factors as pump calibration errors and CT variations. When sampling field atmospheres another potential source of error is introduced — concentration gradients. These factors could account for large differences in concentration occasionally observed between the CT's and passive monitors. Although comparisons to the CT as the "true value" may not present passive monitor results in their true light, the CT sampling method remains the standard procedure for collecting time-weighted average concentrations of TCE and MC and provides one means for evaluating the use of the monitors under field conditions.

Conclusion

As evidenced by the comparison data, both 3M and DuPont passive monitors appear to provide a viable means of collecting MC and TCE at vapor degreasing sites. When evaluated in the laboratory, both passive monitors were in good agreement with the theoretical concentrations of both ana-

lytes. In the field, the devices generally compared favorably with charcoal tubes and each other. In isolated cases where the passive monitors and CT's disagreed, the source of error could not be positively defined. These discrepancies could possibly be attributed to the inability to locate different samplers in the "same" atmosphere and or the combined imprecision of both sampling techniques.

At concentration levels not exceeding MC and TCE TLV's, both passive monitors can be used for 8 hour sampling periods without being overloaded. If high concentrations are expected, sequential sampling for shorter periods of time are recommended.

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The use of passive organic vap r monitors has been suggested as an alternative to the use of charcoal tubes with a portable pump as a method t assess a worker's exposure to organic compounds. This study simultaneously ompares DuPont's, Abcor's, and 3M's passive monitors to the charcoal tube method. The study us d a ll-characterized dynamic exposure system to closely duplicate actual environmental exposure conditions. The vent vapor generation system provid d accurate, stable, and reproducible atmospheres within the exposure chamber. This total system is recommended as a significant improvement over previously reported techniques. Temperature, relative humidity, barometric pressure and air velocity were monitored and held within a small range of variation. Desorption efficiencies were determined for each of the organic compounds on each of the sampling devices used. Statistical analysis determined monitor performance. All three manufacturer's monitors are demonstrated to be an acceptable alternative to the use of charcoal tubes. Several modifications are suggested concerning analysis of these devices. A problem in monitor performance is noted.

A dynamic-flow chamber comparison of three passive organic vapor monitors with charcoal tubes under single and multiple solvent exposure conditions

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Introduction

The Occupational Safety and Health Administration has required industry to monitor workers' exposures to various organic compounds and has established permissible levels to minimize possible ill-effects to workers exposed to these chemicals. These exposures are expressed as a time-weighted average (TWA).

When these limits were first established, the National Institute for Occupational Safety and Health (NIOSH) recommended the collection of organic vapors on a charcoal tube using a calibrated pump. The charcoal in these tubes was then analyzed using gas chromatography. This technique has been extensively tested and reported in the literature, and has become the routine collection method for organic vapors.[1-10]

New methods of collection have been developed which rely on passive organic vapor dosimeters. These monitors do not require a mechanical pump, but rather use the diffusion principle as the driving force in sample collection. Abcor's Gasbadge, 3M's 3500 organic monitor, with draft shields, and DuPont's Pro-Tek, without any shield, use this principle.

Previous studies to evaluate these dosimeters have been limited in scope because of one-to-one comparisons of charcoal tubes to passive organic vapor monitors. The majority of studies have employed field monitoring[11,12] and have been of limited value because of many uncontrolled parameters complicating interpretation.

The few laboratory controlled studies have restricted themselves to the use of static[13,14] or quasi-dynamic[15] systems to expose these monitors. These exposure systems have several drawbacks which are minimized by the use of dynamic systems with larger exposure chambers and a flow-through design which minimizes the "wall effects" found in many smaller static systems. A constant supply of organic vapors provides a stable concentration which is not reduced as the monitors collect the solvent. In static systems, this reduction can affect chamber concentration significantly at low concentrations.

The study reported here compares the charcoal tube method to passive dosimeters of three major manufacturers: DuPont's Pro-Tek, Abcor's Gasbadge, and 3M's 3500 Organic Vapor Monitor; using a dynamic exposure system capable of generation of organic solvents over a wide range of concentrations. The resulting atmospheres are stable and reproducible. Other parameters known or suspected to interfere with these dosimeters, such as relative humidity, temperature, air velocity, and barometric pressure were monitored and remained within a small range of variation so as to minimize their effects.

methods and procedures

exposure chamber

Exposures were performed in a 0.25M^3 Rochester type dynamic flow inhalation chamber constructed of plexiglass. Units of this design are used almost universally for inhalation toxicology studies. Characteristics of these chambers, in terms of uniformity of air flow and contaminant concentra-

The conclusions and suggestions incorporated in this paper are solely those of the above authors. No part of this paper was edited or revised by any of the three corporations which participated in this study. The three corporations were given a copy of the completed manuscript and asked to present their opinions, if any, to be included in the comments.

tion throughout, are widely documented.[16,17] A vacuum system at the exhaust port created a negative pressure flow system. A Magnehelic gauge installed at this point measured the total flow rate in the chamber, which was controlled by a gate valve. The Magnehelic gauge was calibrated for flow using a 120 liter gas spirometer. A curve relating flow to gauge setting was prepared. This correlated significantly to the theoretical flows calculated for the various differential pressures. A chamber flow of 250 liters per minute (Lpm) was chosen and the corresponding value was set and monitored using the Magnehelic gauge. The chamber's relative humidity and temperature were monitored with an Abbeon Certified Hygrometer and temperature indicator.

A 2.5 cm (1 in) mesh wire was suspended 15.2 cm (6 in) below the top of the chamber and the badges were suspended at eight selected positions 5.1 cm (2 in) below this screen. Thus, all badges to be tested were located on a cross-sectional plane approximately 10.2 cm (4 in) above the mid-section of the chamber. Badges were placed a minimum of 15.2 cm (6 in) apart. In addition to the velocity of test atmosphere provided by the one change per minute (250 Lpm) flow through the chamber, air movement within the chamber was augmented using two 20.3 cm (8 in) fans installed in the upper dome of the chamber. Air velocities at all badge positions were measured with a Kurtz air velocity meter and determined to be greater than 100 fpm at each position.

A 30.5 cm (12 in) stainless steel needle was installed in the chamber and, when attached to a series A-2 Precision Sampling gas syringe, was capable of sampling the atmosphere at positions adjacent to the badges being exposed.

olvent generation system

The solvent generation system employed the principle of a constant vapor concentration at a constant temperature and pressure. The constants for vapor pressure calculations were obtained for the four solvents[18] and their saturated vapor concentrations were determined at 0 °C and 760 mm Hg. By knowing this, and setting the total exposure chamber flow at 250 Lpm, one may calculate the flow necessary for generating 10 and 100 parts per million (ppm). This system was similar to that employed to make the NIOSH Proficiency Analytical Testing Program samples.[19] These flows were acheived using cylinders of purified nitrogen equipped with 2-stage regulators to reduce the pressure to a moderate level. The final flows were individually regulated with a blunt needle valve for each solvent and these flows were monitored by differential pressure manometers equipped with variable orifices and standard manometer fluid. The nitrogen was then directed into gas washing bottles containing each solvent and the saturated vapor was directed into the intake port of the exposure chamber. The solvents in the gas washing bottles were maintained at a constant temperature with an ice-water bath at equilibrium. Figure 1 depicts the exposure chamber and solvent generation system.

analytical conditions

[redacted] analytic determinations were performed on a Perkin [redacted]mer 3920 gas chromatograph equipped with a Supelco 3.05 m (10 ft) glass column, 2 mm ID, silane treated and packed with 10% FFAP on 80/100 mesh chromasorb W AW.[1,6,8,10,15] The operating temperatures were set as follows: 160 °C at the injection port, 220 °C at the detector, and 100 °C isothermal column operation. Chromatographic grade nitrogen was used as the carrier gas and the flow was set at 30 cc/min. A flame ionization detector was used. Maximum sensitivity of this detector was determined following the manufacturer's recommended steady state method. The settings determined were 16 pounds per square inch (psi) for the hydrogen and 60 psi for the zero air.

Samples were introduced into the instrument in two ways. Liquid samples were injected following the method recommended by NIOSH.[1,6,10] A Glenco 10 μL syringe is flushed with carbon disulfide several times and 3 μL of carbon disulfide is drawn into the syringe. Then 0.2 μL of air is drawn into the syringe to be used as a marker. Finally, a 5 μL aliquot of sample is drawn into the syringe and the plunger is retracted further to prevent evaporation at the end of the needle.

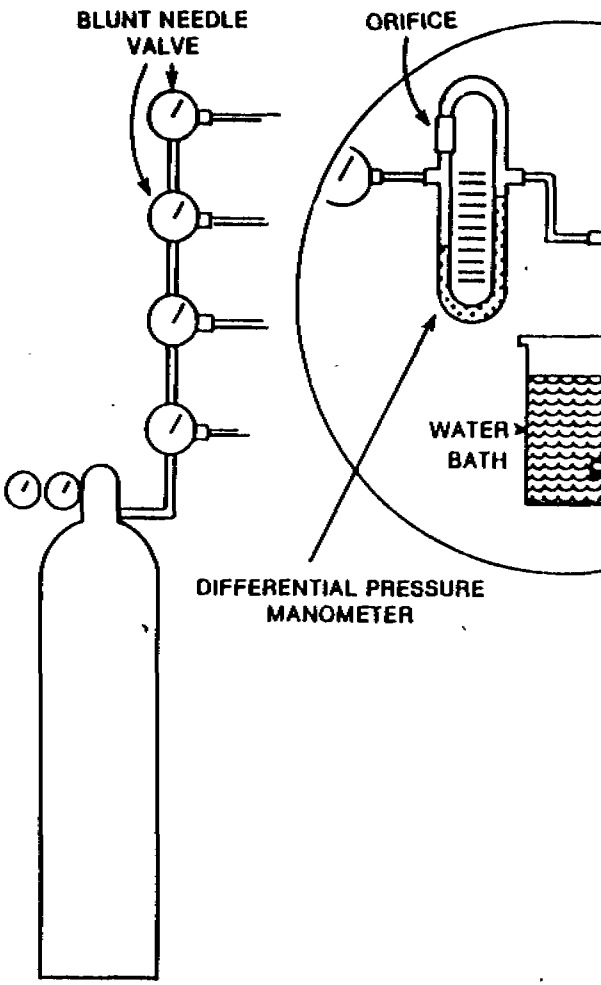
Air standards and chamber samples were collected with a Precision Sampling Pressure-Lok Series A-2 1.0 mL syringe. Samples were collected with 30.5 cm (12 in) needles compatible with this syringe. The plunger was slowly and completely withdrawn and the syringe flushed. This step was repeated, a sample taken, and the syringe valve was closed. The needle was removed and a 5.1 cm (2 in) needle attached. The valve was reopened, the volume was reduced to 1.0 mL, the valve was closed and the plunger was depressed to 0.2 mL. The needle was then inserted through the septum of the gas chromatograph, the valve was opened and the plunger was simultaneously depressed.

All determinations were made using the peak height as a direct indication of peak area due to the high resolution and narrow width of the peaks.

validation of chamber atmosphere stability

Exposures were conducted to test the temporal stability of the exposure conditions. These exposures were monitored by discrete grab samples which were analyzed by gas chromatography. The variability of chamber concentration for each solvent at both low and high concentrations over six hour intervals was determined. Mean concentrations and standard deviations were determined and are presented in Table I.

Two preliminary studies were conducted to verify uniformity of chamber concentrations and reconfirm that no significant concentration gradients existed in the plane of exposure. For one of the solvents used in this study (trichloroethylene), mean values were determined for 10 positions across a plane in the chamber, each position sampled 3 to 5 times. Relative results of these 10 values gave a mean of 2650 ppm with a standard deviation of 2.9%. Using trichloroethylene for a second series, four points (sampling each position 4 to 5 times) gave a mean value of 3400 ppm with a standard deviation of 0.5%. This degree of uniformity has been a common experience of this laboratory with these chambers in past studies.



CYLINDER OF PREPURIFIED NITROGEN WITH 2-STAGE REGULATOR

EXPOSURE SYSTEM

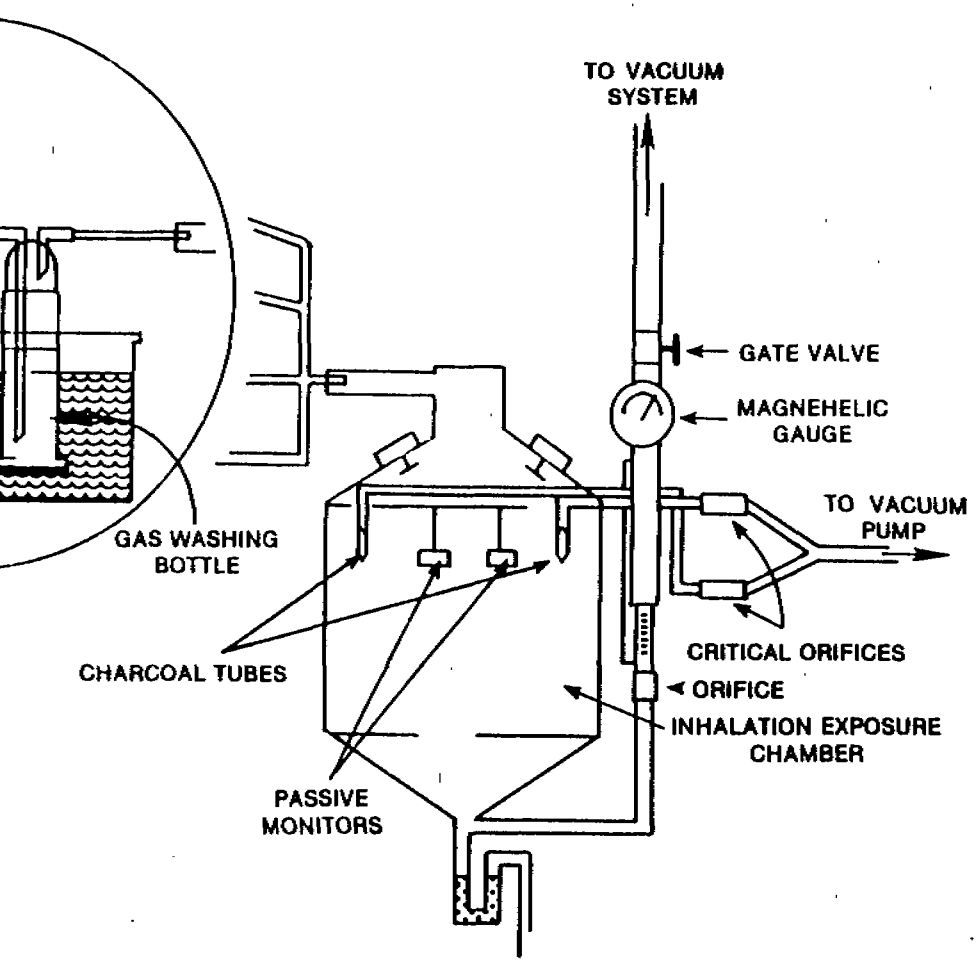


Figure 1 — Exposure system.

determination of desorption efficiencies

Desorption efficiencies for the charcoal tubes and all three manufacturer's dosimeters followed the same basic steps outlined in NIOSH P and CAM 127 (subject to the modifications by each manufacturer).

Placing the charcoal or collection element in a septum capped vial, the analyst injected the solvent(s) of interest onto the collection medium. The sample was allowed to stand overnight. The following day the appropriate amount of carbon disulfide solution was added, the sample gently agitated for 30 minutes and an aliquot injected into a gas chromatograph. Standards and blanks were treated similarly. Desorption efficiencies were determined using the equation:

$$\text{desorption efficiency} = \frac{\text{area sample} - \text{area blank}}{\text{area standard}}$$

All corrected sample values were divided by each of the standard values and these were averaged to give the most representative desorption efficiency for each solvent.

Desorption of all solvents on all collection mediums was accomplished using a solution of 3% n-butanol in carbon disulfide. This is recommended by NIOSH and Abcor to improve the recovery of isopropanol.[2] All standards and samples were run a minimum of five times each and averaged to accurately reflect the actual value.

Desorption efficiencies for the charcoal tubes were performed first. A 100 mg sample of charcoal from the charcoal tubes was placed into a 1.0 mL mini-vial and capped using microsep F-138 teflon lined septa, the solvent was then injected into the charcoal. The amount used was determined "to represent that present in a 10-liter sample at a concentration equal to the federal standard."[1] Four samples and two blanks were prepared for each solvent and allowed to stand overnight. These samples were desorbed by injecting 1.0 mL of the carbon disulfide solution into each sample. Duplicate standards were made for each solvent by injecting 10 times the amount used on the samples into 10 mL of carbon disulfide.

The desorption efficiencies for each of the four solvents on the charcoal tubes were determined separately twice. A mixture of these four solvents, in the same volume to volume proportions, was prepared and the amount used for the multiple solvent samples was equal to the sum of the volumes used for each of the previous single solvent samples. A statistical analysis of the desorption efficiencies determined by this method showed no difference between those determined one at a time.[6] Therefore, to conserve time and collection elements this later method was adopted for the rest of the determinations.

Desorption efficiencies for Abcor were determined similarly. The collection elements were placed in the vials provided by Abcor. These elements become overloaded at 15 mg of solvent so 13 μL of the solvent mix was used (11.4 mg) to prepare each sample. Private correspondence with Abcor recommended using 3.0 mL of the CS_2 solution for desorption.[21] Standards were prepared by injecting 43.3 μL of mix ($13 \times 10/3$) into 10 mL of CS_2. Two standards and four samples were run.

Desorption efficiencies for the DuPont badges were determined by placing the collection elements into 2.0 mL mini-vials. 26 μL of the solvent mix was used to prepare each sample. Three standards and four samples were run.

3M recommends that the CS_2 solution be placed into their badges and samples be withdrawn directly. This method was difficult to reproduce and the desorption efficiencies determined were much higher than 100% due to the large amount of air space within the badge. To determine the desorption efficiencies for the 3M badge, the collection element was removed and placed into a 2.0 mL mini-vial. 3M recommends the amount of solvent used be determined by the amount of solvent present in a 7-liter sample at one-half the TLV. This was determined to be equivalent to 9.1 μL of the solvent mixture. The lowest overload value reported was 8.5 mg for hexane and the total for the 9.1 μL was 7.9 mg. Standards were prepared by injecting 60.7 μL of the solvent mix into 10 mL CS_2. A 1.5 mL aliquot of the CS_2 solution was used to desorb the elements, as recommended by 3M. Three standards and three samples were run.

For all analyses, the attenuation was adjusted for each compound to provide for a reasonable peak height. The desorption efficiencies which were determined are presented in Table II.

exposure procedures

This study consisted of sixteen exposures, each run included duplicate sampling using both charcoal tubes and each of the three brands of passive monitors.

Eight positions were selected within the chamber at the cross-sectional plane described above. Constraints were imposed that badges should be separated from each other and the walls by 15.2 cm (6 in.) and air velocity should equal or exceed 0.508 m/s (100 fpm). This specific velocity was recommended in NIOSH's protocol for the evaluation of

TABLE I
Chamber Stability

Compound	Concentration (ppm)	
Hexane	17.0 ± 0.5 (n=27)	91 ± 2 (n=35)
Isopropanol	13.6 ± 0.6 (n=19)	76 ± 2 (n=35)
Trichloroethylene	14.3 ± 0.4 (n=34)	89 ± 2 (n=23)
Toluene	13.9 ± 0.7 (n=35)	102 ± 2 (n=23)

TABLE II
Desorption Efficiencies for Various Organic Vapor Monitors

Compound	Charcoal Tube	Passive Monitors		
		DuPont	Abcor	3M
Hexane	1.02	1.02	1.01	0.96
Isopropanol	0.98	0.71	0.93	0.85
Trichloroethylene	1.03	0.96	1.02	0.95
Toluene	1.01	0.94	1.01	0.96

TABLE III
Summary of Statistical Analysis Comparing Charcoal Tub vs. Passive Monitors[A]

	Intercept			Slope			r^2	n
	Estimated Intercept (a)	Standard Deviation	t_0[B]	Estimated Slope (b)	Standard Deviation	t_1[C]	Corrected	
DuPont								
Hexane	−0.136	0.137	−1.00	1.0568	0.0791	0.72	0.903	20
Isopropanol	−0.1179	0.0902	−1.31	1.1292	0.0584	2.21[D]	0.952	20
Trichloroethylene	0.1168	0.0412	2.84[D]	0.9478	0.0276	−1.89	0.984	20
Toluene	0.0159	0.0405	0.39	0.9610	0.0262	−1.49	0.986	20
Abcor								
Hexane	−0.215	0.100	−2.14[D]	1.1210	0.0602	2.01	0.953	18
Isopropanol	0.396	0.130	3.05[E]	0.8429	0.0848	−1.85	0.852	18
Trichloroethylene	0.1474	0.0520	2.83[D]	0.9140	0.0357	−2.41[D]	0.975	18
Toluene	0.0191	0.0328	0.58	0.9644	0.0208	−1.71	0.992	18
3M								
Hexane	−0.1514	0.0900	−1.68	1.0772	0.0527	1.46	0.956	20
Isopropanol	−0.0437	0.0613	−0.71	1.0009	0.0367	0.02	0.975	20
Trichloroethylene	0.0560	0.0303	1.85	0.9318	0.0191	−3.57[E]	0.992	20
Toluene	−0.0096	0.0293	−0.33	0.9811	0.0190	−0.99	0.993	20

[A]Data were analyzed using the model $\log y = a + b \log x$

[B] $t_0 = \frac{a - 0}{S.D.\ a}$

[C] $t_1 = \frac{b - 1}{S.D.\ b}$

[D]Statistically significant at $p < .05$

[E]Statistically significant at $p < .01$

...e dosimeters.[20] Manufacturers' criteria establishes a m...um velocity exposure well below the velocity used in this study.[22]

At two of the locations in the chamber, charcoal tubes were placed in a vertical position and tubing was run to the outside of the chamber to a vacuum pump. Critical orifices were made, calibrated, and installed in these lines to accurately control the sampling rates of the charcoal tubes at 0.294 and 0.286 Lpm. A single charcoal tube was used at each position for the single solvent low concentration exposures, two for the single solvent high concentration (three for isopropanol), and four for the mixed exposures. These charcoal tubes were changed at regular intervals to prevent overloading and loss of sample. To ensure complete collection, four charcoal tubes were joined in series to sample during each of the two spiked exposures.

Placement of the passive monitors at the other six positions was randomly determined prior to the first exposure and then held constant for subsequent exposures. The rationale for this was based on the previously determined uniformity of solvent concentration across the plane of exposure.

The first four exposures were low concentration (approximately 10 ppm), and of six hours duration: each exposure utilizing one of the four solvents from this study. To determine the required flows of organic solvents to the chamber ...cessary to achieve the desired concentrations, a series of ...ds was prepared. A curve was established which rela... concentration to peak height and the appropriate peak height representing a 10 ppm concentration was determined. Flows to the chamber were adjusted until the sample obtained duplicated this peak. The standards used for this series of exposures were made at 5, 10, and 15 ppm. These standards were prepared by injecting solvents into calibrated, sealed 20 L pyrex bottles. This container was fitted with a 30.5 cm (12 in) stainless steel needle. A 1.0 mL Series A-2 Precision gas sampling syringe was used to sample these standards.

The second four exposures were high concentration (approximately 100 ppm), and of six hours duration: each exposure utilizing one of the four solvents from this study. The procedure was the same as above, using standards of 50 and 100 ppm.

The third series consisted of six exposures. Each exposure was six hours in duration, with two solvents at the low concentration and two solvents at the high concentration. All six possible combinations were used. Flows were set using the volume which best reflected the above single solvent exposures on the differential orifice manometers. Standards were made at 10 and 100 ppm for this series.

Two final exposures were conducted to evaluate the effect of a short interval, high solvent concentration on a generally low background concentration exposure sequence since it was considered that the time of the spike might influence the apparent performance of the passive monitors relative to the performance of the charcoal tubes. These exposures involved subjecting the monitors for six hours to all four solvents at a low background level on which a spiked concentration was imposed for 36 minutes. The first of these exposures

involved spiking one hour after the start of the run while the second exposure involved spiking just prior to the last hour of the run. Solvent concentrations for both the background and spike were established solely by consideration of total monitor loading to preclude saturation. These concentrations were in the range of 10 and 100 ppm, respectively.

calculations

Exposures were conducted in the four groups as mentioned in the exposure procedures section. The exposed charcoal tubes and monitors were removed immediately from the chamber after the six-hour exposure, sealed according to the appropriate manufacturer's instructions, and refrigerated at 2-4 °C for up to two weeks prior to analysis.

After each group of exposures had been completed, the samples were analyzed using the procedures previously described. Samples were analyzed three to five times each and averaged to reduce possible error. A series of standards was prepared in concentrations spanning the range of loadings for each monitor and analyzed each day with the samples.

For each day of analysis, a curve relating chromatographic peak height to concentration of the standards was determined by linear regression with the restriction the line must pass through the origin. There were several reasons for this restriction. Theoretically, the curve should pass through this point and the higher the concentration of the standards the more accurately the standard could be made. Also, when certain combinations of two solvents at high concentration and two at low concentration occurred, attenuation could not be adjusted to give a large peak for all four compounds because of dramatic shifting in the baseline. Peaks smaller in size but with a stable baseline were preferred. For smaller peaks, a small change in the y-intercept could cause a large change in the calculated value for the monitor. This limitation was most pronounced for Abcor's and 3M's monitors because of the lower loadings and larger amounts of carbon disulfide used to desorb the samples. Calculations to determine average exposures in ppm were carried out using the equations supplied by each manufacturer.

TABLE IV
Comparison of Results by Chamber Position

Compound	Charcoal Tube			DuPont Monitor		
	4>2[A]	n	p Value[B]	6>3[C]	n	p Value[B]
Hexane	6	10	.754	0	9	0.004
Isopropanol	4	10	.754	0	9	0.004
Trichloroethylene	4	10	.754	0	9	0.004
Toluene	6	10	.754	1	9	0.039

[A]Number of exposures where the value at position 4 was greater than the value at position 2.

[B]Two-tailed sign test.

[C]Number of exposures where the value at position 6 was greater than the value at position 3.

statistical analyses

Separate comparison was made between the average of the charcoal tube values and each of the values from both of the passive monitors. Linear regression was used to compare the data. The model: $\log y = a+b \log x$ was chosen, with y reflecting data from the charcoal tubes and x reflecting data from the passive monitors. As the concentration of a solvent increased the absolute variation also increased. By the use of logarithms, this phenomenon became more pronounced. Zero values were omitted for this analysis. The results of these calculations are shown in Table III. Separate comparisons were made between the average of the charcoal tube values and the higher value in each pair of values for the passive monitors and then repeated using the lower value of each pair. These sets of analyses gave results similar to the analysis encompassing all the data.

Values for the charcoal tubes and DuPont's monitors were tested to determine if chamber position affected sampler performance. This determination was made using the sign test. The results of this are presented in Table IV.

results

Table I shows the results of testing the stability of the solvent atmospheres generated for the exposure chamber.

Temperature, relative humidity and barometric pressure were monitored for the sixteen exposures in this study. Mean values for these chamber parameters were: temperature 23.2 °C (with a standard deviation of 1.1 °C), 46% relative humidity (with a standard deviation of 7%), and 752 mm Hg barometric pressure (with a standard deviation of 3 mm Hg).

The results of determining desorption efficiencies are presented in Table II. Comparison of individual passive monitor performance to charcoal tube performance is presented in Table III. Comparison of results by chamber position are presented in Table IV. Data for the series of the sixteen exposures which were used in the statistical analysis of this paper can be found in Appendix "A" of the unpublished master's thesis.[21]

discussion

Chamber atmospheres were monitored for six hours for each solvent at both low and high concentrations to determine the temporal stability of the system. The results are presented in Table I. Absolute variability increased as the concentration increased while relative variability remained within ± 5%. Results of the preliminary studies on the planar uniformity of atmospheres are indicative of the performance of these chambers, the design of which has been used routinely in toxicology investigations for over 30 years. The results demonstrated by this investigation show the feasibility and desirability of generating organic solvent atmospheres for exposure chambers by the system described in this study.

Desorption efficiencies were determined for each solvent for each monitoring device and are presented in Table II. Desorption efficiencies determined on charcoal tubes were

individually compared against those determined in a matrix and no significant difference was found. This finding had been reported earlier.[6] The desorption efficiencies for all the passive monitors were determined for all solvents simultaneously.

Desorption efficiencies for DuPont were run twice to confirm the low desorption efficiency determined for isopropanol. Seventy-one percent was determined each time and was accepted because of its reproducibility.

Determination of desorption efficiencies for the 3M monitors was attempted twice using the 3M recommended method. Results were consistently above 100% recovery. No problems were experienced when the charcoal pads were removed from the badges and analyzed in 2 mL vials.

In cases where there are solvents at both high and low concentrations, it is difficult to change attenuation on the gas chromatograph to give a large peak due to dramatic shifting in the baseline. This limitation was most pronounced for Abcor's and 3M's monitors due to the lower loadings and larger amounts of carbon disulfide used. Loadings, because of higher concentrations of other solvents, could not be increased without overloading the monitors.

Since the peaks for some of the compounds were small, a change in the y-intercept could cause a large change in the value calculated for the monitor. Therefore, the standard curves were calculated with the restriction that the curve pass through the origin. Theoretically, the line should pass through this point. In addition, standards prepared at low concentrations could not be made with as much accuracy as those at higher concentrations. This made it difficult to determine where the curve should pass at the lower end of these curves.

Because of the problems encountered with solvents at these lower concentrations it is suggested that smaller amounts of carbon disulfide be used for desorption. The slight increase in desorption efficiency does not appear to outweigh the disadvantage of smaller peaks.

Difficulties were also encountered at lower concentrations with the quantification of isopropanol due to a severe interference by carbon disulfide which made baseline determinations difficult. If this problem is expected, analysis by a different chromatographic column, which will give better resolution, is recommended.

Exposures within the chamber were all conducted with air velocities in excess of 0.508 m/s (100 fpm) as is recommended by NIOSH. DuPont stated that for the testing of their Pro-Tek organic vapor monitors, their badges were more sensitive to inadequate face velocities than Abcor's or 3M's monitors.[22] For this reason, DuPont's badges were placed at the two positions with the highest velocity. One position averaged 0.762 m/s (150 fpm) and the other position averaged 0.635 m/s (125 fpm). No difference was expected since DuPont stated these monitors were calibrated to accurately measure between 0.169 m/s and 2.032 m/s (35 to 400 fpm). After analysis of the first four exposures, a noticable difference in values was observed. Positions of the DuPont monitors were recorded for the last twelve exposures. Results by position were compared for charcoal tubes and the DuPont monitors. These results are presented in Table IV. It is clear that there is no significant difference in positions for the charcoal tubes while there is a significant difference in position demonstrated for the DuPont monitors. It appears that these monitors are sensitive to differences in velocities of the surrounding air since all other variables were kept constant at both positions. These monitors, unlike Abcor's and 3M's monitors, do not have a draft shield. This could explain the difference in monitor performance. It is also possible that chamber concentration at these locations varied since they were not monitored during actual exposures. Data previously presented on uniformity of solvent concentration within the chamber minimize this as a possible explanation. It should be emphasized that positions were not recorded for the Abcor and 3M monitors and therfore similar comparisons could not be made.

Comparison of monitor performance to charcoal tube performance is the most widely recognized method for validation of passive monitors. Comparison was made using the model: $\log y = a + b \log x$ where the y value was the average value for the charcoal tubes which was paired against each of the values calculated from the passive monitors for the same exposure. This series is summarized in Table III. Comparison was repeated using the average value for the charcoal tubes and the higher value in each pair for each organic monitor. Comparison was made substituting the lower values for the higher. Little difference was noted for these three series of analysis which demonstrated both organic vapor monitors and charcoal tubes would give a good representation of the exposure. Table III shows that all three brands of passive monitors should be considered an acceptable alternative to the recognized charcoal tube method. All three companies' monitors had y-intercepts close to the origin. For the determination of higher concentrations closer to the TWA's of these compounds, the slope of the regression line becomes increasingly important. While all three companies' monitors have fairly good correlations with the results from the charcoal tubes. 3M's monitor gave the best slope in two out of four cases and showed the smallest variation every time as is demonstrated by examination of the standard deviation. 3M's monitor did not perform as well as DuPont's monitor for trichloroethylene and hexane. A poor correlation between charcoal tubes and Abcor's monitors pertaining to isopropanol could be due to problems with baseline determination discussed earlier.

conclusions

1. Under conditions similar to those of this study, DuPont's, Abcor's, and 3M's passive organic vapor monitors are an acceptable alternate to the charcoal tube method for assessment of a worker's exposure to organic solvents, as is demonstrated by the good correlation between each monitor with the results obtained by the charcoal tubes.

2. Significant differences between monitor performance were noted for DuPont's monitors. Sensitiv-

ity to velocities surrounding the monitor is suspected as the reason.

3. When isopropanol is monitored at low concentrations, especially in the presence of high concentrations of other compounds, selection of chromatographic columns becomes important if one wishes to minimize interference by carbon disulfide.
4. Analysis of 3M's monitors is improved by removing the charcoal pad and placing it into a 2 mL septum capped vial.
5. Desorption efficiencies can be determined for several solvents simultaneously with no significant difference over determination of each solvent individually, provided the charcoal device is not over-loaded with solvents.
6. The exposure system, including the organic solvent generation system described in this paper, is recommended as a significant improvement over previously reported exposure techniques for the determination of monitor performance.

It should be emphasized that this study was a laboratory controlled experiment which, while examining several important parameters, kept several other equally important parameters constant. The conclusions drawn in this paper should only be considered valid when the conditions of exposure have been met. This is the first of what should be a series of studies which need to be conducted to verify whether these conclusions can be extended to conditions such as elevated relative humidity and extremes temperature.

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The history of development and validation testing of passive dosimeters is reviewed. Theoretical consideration including possible limiting factors or interferences, are presented. Laboratory and field validation tests ar critically reviewed and results ar presented for comparative purposes. Evaluation of available data indicates tha passive dosimetry, with some exceptions, is an acceptable method for monitoring gasses and vapors. Mo importantly, passive systems appear to be as reliable as the now accepted active sampling systems.

Passive dosimetry — state of the art review

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introduction

Recognition, evaluation and control are the cornerstones of the application of that mixture of science and art known as industrial hygiene. These three tasks, however, are no longer the eminent domain of the industrial hygienist. In the past decade, a proliferation of training in the recognition of workplace hazards has been made widely available to workers and management alike. At the other end of the spectrum has been the training of individuals highly specialized in the control of specific hazards, especially those involving noise and toxic air contaminants. These developments are welcomed because they contribute significantly to the ultimate goal of protecting the health of workers by providing safer and more healthful workplaces.

At the same time, professional industrial hygienists recognize that often the critical step in the process is not recognition of toxicity, but evaluation of hazard which leads to the subsequent development of the most effective means of control where warranted. This key step of evaluation is the unique domain of the industrial hygienist, often supplemented by other members of the occupational health and safety team. Where evaluation requires the determination of worker exposure to airborne toxic substances, the industrial hygienist has seen a revolution in the development of sophisticated techniques and equipment.

The "organ-grinder" impinger sampler is a relic, having been replaced by constant flow, eight-hour battery-operated pumps, light enough to be carried by the worker. The liquid bubbler and impinger have been replaced by the charcoal and chemical substrate sampling tube. The laboratory has come to the field in the form of the portable gas chromatograph and infrared monitor, albeit with a price rise directly proportional to the sophistication of the equipment. Even the once lowly, direct-reading detector tube has become legitimate with the establishment of government programs to certify accuracy and precision.

But while most evaluation techniques were reaching the point where the industrial hygiene staff required the addition of someone with a Ph.D. in electrical engineering, a new device has appeared which has the key of simplicity — the personal passive dosimeter: personal, because it can be wor by the worker in close proximity to the breathing zon passive, because there is no pump to move the air over collector, which equates to fewer calibration and mainte nance problems. Some quarrel with the term dosimeter, wit purists preferring to call them collectors, monitors, o samplers. While many of the devices are collectors an require the application of subsequent analytical procedure others provide for a more direct measurement of "exposur dose." Their basic appeal, however, is simplicity of use Theoretically, elaborate calibration procedures are unneces sary, and all that is needed is a fairly reliable timepiece t measure exposure duration. There is some recognition tha temperature and humidity may affect the observations therefore, most manufacturers advise the user to report thes environmental conditions to the analytical laboratory pro cessing the dosimeter.

Rather than viewing passive dosimeters as another way t replace the industrial hygienist, industrial hygienists mus recognize and appreciate the potential of the dosimeters i helping to achieve the hygienists' goals. That potential i significant in that personal dosimeters, if properly used offer the opportunity to revolutionize the evaluation step The parallels with detector tubes, as well as with noise and ionizing radiation dosimeters, are obvious. Indeed, th parallel with radiation dosimeters, especially film badges i striking. The opportunity to significantly expand the mea surement of worker exposure to many toxic materials can provide a quantum leap in our ability to provide safe and healthful workplaces. With any sampling device, however there also must be the understanding that use of such device is only one part of the evaluation step. The concepts o proper selection of workers at risk; the understanding o limitations, interferences and similar factors, and ultimately the proper interpretation of the results are still key ingre dients in the evaluation step. The possibility of "false nega tive" decisions leading to erroneous assumptions of safety or "false positive" conclusions leading to unwarranted expenditures of resources for controls, still exists regardless of the measurement device used.

With the rapid proliferation of passive dosimeters in the past several years, it is appropriate that industrial hygienists evaluate the "state-of-the-art" and, as professionals, become involved with the proper application of these monitoring devices.

theori s of operation

In that passive dosimeters by definition do not use an air moving device to transport contaminated air to a collector, natural forces are relied upon to ensure that a representative amount of contaminant is "seen" by the detector. To date, one of two principles has been applied in the design of dosimeters. The first, and most widely used, is the principle of *diffusion* of contaminant molecules through a stagnant gas (air) layer. The second principle involves the absorption in and subsequent *permeation* of contaminant molecules through a membrane.

Diffusional monitors rely on the movement of contaminant molecules across a concentration gradient which for steady-state conditions, can be defined by Fick's First Law of Diffusion [1]

$$W = -DA\frac{dc}{dx} \tag{1}$$

where: W = mass transfer rate, ng sec.
D = diffusion coefficient, cm^2 sec.
A = cross sectional area of diffusion path, cm^2, and
dc dx = the instantaneous rate of change in concentration over diffusion path, (ng cm^3)cm^{-1}.

Considering the change in concentration ($C_1 - C_0$) over the total diffusion path length ($X_1 - X_0 = -l$), equation (1) becomes,

$$W = D\frac{A}{l}(C_1 - C_0) \tag{2}$$

where, l. = length of the diffusion (static) path, cm.
C_1 = ambient concentration of contaminant, ng cm^{-3}, and
C_0 = concentration of contaminant at collecting surface, ng cm^{-3}.

If an effective collection medium is employed, the contaminant concentration at the surface of the collector (C_0) can be assumed to be zero, and multiplying both sides of equation (2) by time, yields

$$M = D\frac{A}{l}(C_1)t \tag{3}$$

where: M = total mass transferred, ng, and
t = time that the badge is exposed to the contaminated air, sec.

It is also interesting to note that the units of the product of D and A, divided by l., are cm^3 sec. which are the same units associated with active air-moving devices such as personal sampling pumps.

Rearranging equation (3) as follows:

$$C_1 = \frac{Ml}{DAt} \tag{4}$$

it becomes apparent that five factors affect the measurement of the ambient air concentration of a substance (C_1). Two of the factors (l. and A) are physical parameters associated with the construction of the dosimeter, one (M) is provided by measuring the total mass of contaminant collected by the sampler, another is the duration (t) the sampler was exposed to the contaminated atmosphere, and the final factor (D) is an individual property of each vapor or gas. It also is known[1] that the diffusion coefficient is directly proportional to the absolute temperature (T) of the vapor, raised to three-halves power and inversely proportional to the atmospheric pressure (P).

$$D\alpha\frac{T^{1.5}}{P} \tag{5}$$

Dosimeters that rely on the principle of *permeation* through a membrane are especially useful where the contaminant of concern is usually found mixed with other interfering vapors or gases or when a liquid collecting medium is employed. The goal then becomes to identify a membrane material that is highly permeable to the contaminant of interest and impermeable to most other components in the atmosphere, and or the collecting media.

The determination of ambient concentrations of a contaminant using a permeation device can be determined from the formula:

$$C = wk\,t \tag{6}$$

where: C = concentration of contaminant, ppm.
w = mass of contaminant collected, μg.
k = permeation constant, ppm-hours μg, and
t = exposure time, hours.

The permeation constant (k) is determined experimentally and is a function of the specific membrane material and contaminant of interest.[2]

sources of measurement error

The most obvious sources of error for both types of passive dosimeters are apparent from equations (4) and (6). Common to both badges are determinations of the mass of contaminant collected and the time of exposure of the dosimeter to the contaminated atmosphere. For the diffusional monitor, accurate knowledge of the physical parameters associated with badge construction (length and cross-sectional area) and the diffusion coefficient of the contaminant are important. There are at least nine prediction methods for calculating the diffusion coefficient, and in one study comparing observed and expected values for more than 100 compounds it was not uncommon to have less than 50 percent of the calculated results within ± 5 percent of the observed.[3] Montalvo has described a procedure for limiting errors associated with computed diffusion coefficients.[4] At

least one manufacturer, the 3M Company, makes available its procedures for determining sampling rates (DA, L) for its badges.[5] Its approach has been to experimentally determine the sampling rate for five or six compounds in a chemical family to establish the relationship between the diffusion coefficient and the measured sampling rates. Sampling rates for other compounds are determined from the diffusion coefficients calculated by the Hirschfelder equation and the empirical relationships developed from the test compounds. The rationale for the selection of the Hirschfelder equation is not given, but in the study of the nine diffusion coefficient formulas, the author concluded that for higher molecular weight compounds the Hirschfelder, Biard and Spatz equations were in closest agreement with determined values.[3] For the permeation monitor, accurate determination of the permeation coefficient for each monitor is necessary for obtaining accurate results. Factors influencing permeation include: thickness and uniformity of the membrane, affinity of the membrane for the analyte, swelling or shrinkage of the membrane, and possible etching by corrosive chemicals.

The problems associated with accurate determinations of the mass of the contaminant collected are similar to those involved with other collection devices such as charcoal or silica gel tubes, or to those in which the collection of the contaminant involves a chemical reaction with the collection medium. Using known amounts or concentrations of contaminants to determine collection and or desorption efficiencies is as critical a step for passive dosimeters as it is for other methods of collection. Saturation of the sorbent as well as the subsequent accuracy of analytical techniques are also part of the total error associated with the measurement.

Another common concern in all types of environmental measurements is the potential for interferences, either positive or negative, from other contaminants in the sampled air. As the evaluation of passive dosimeters has matured, increased attention is being paid to possible interferences in multi-contaminant exposure situations, in both the laboratory and field. In evaluating such interferences it should be recognized that there are several potential sites for such interferences to appear, *e.g.*, effects on adsorption or absorption efficiency of the sampling medium, chemical reactions of two or more contaminants prior to analysis, and the multitude of interferences associated with analysis of complex mixtures of gases and or vapors. These problems also are found in the more classical sampling and analytical methods.

Accurate measurement of the time the sampling device is exposed, is essential to most industrial hygiene sampling procedures. For both short-term and full-shift exposure measurements, errors less than one percent, *i.e.* 9 seconds in 15 minutes and 4.8 minutes over 8 hours, are not unreasonable goals.

For the diffusion coefficient and possibly the permeation constant, it would appear that three factors have the greatest effect on variability. These factors are the two already identified, temperature and pressure, and, less readily apparent, the velocity of the air external to the badges.

Considering temperature and pressure, and referring to equation (5) it can be shown that a temperature rise from 5 to 35 °C would give a 16 percent increase in the diffusion coefficient, while a rise in barometric pressure from 710 to 810 mm Hg would cause a 14 percent decrease.[3] However at the same time, the changes in temperature and pressure also are affecting the concentration (mass volume; actually density is the proper term but most authors use concentration) of the contaminant in that concentration is inversely proportional to the temperature and directly proportional to the pressure. As a result, the total mass (M) collected by the dosimeter is only slightly affected by temperature ($M \propto T^{1/2}$) and is independent of the pressure.[1] Consequently, while at ambient temperatures, the diffusion coefficient will increase about 0.5 percent per °C, and the total mass collected by the sampler will increase less than 0.2 percent per °C. Therefore a temperature change from 25 to 30 °C, if uncorrected, will introduce a measurement error of less than one percent while a change from 5 to 35 °C, if uncorrected, would introduce an error of about five percent.

The final source of error to consider is the velocity of the air external to the dosimeter; often this is referred to as face velocity. In an early assessment of face velocity effects, especially the lack thereof, Tompkins and Goldsmith point out that the important consideration is to contain all resistance to contaminant transport within the stagnant air layer inside the device.[1] As Jonas *et al.* subsequently noted, the face velocity directly affects the concentration gradient $C_1 - C_0$ in equation (2), and C_1 can no longer be assumed to be the ambient concentration when the air external to the badge is stagnant.[6] With zero or low face velocities, the length (L) of the diffusion pathway is effectively extended, and there is a decrease in the measured ambient concentration. In Tompkins' and Goldsmith's work with the GASBADGE™, they determined experimentally that as long as face velocities were greater than 7.5 cm sec (15 fpm) there was "no significant effect on dosimeter response;" however, experimental results supporting this conclusion were not presented.[1] High face velocities may also affect the concentration gradient. Commercially available diffusion devices rely on either a large ratio of diffusion path length to diffusion tube diameter or a wind screen to limit errors from this condition.

One of the most comprehensive tests to document sources of error has been conducted under contract for the National Institute for Occupational Safety and Health, and although concluded, it is not yet available as a public report.[7] The study involved evaluation of the GASBADGE and 3M Organic Vapor Monitor™ (the DuPont badge not being available at the time the study was initiated) via challenge with several organic vapors. The factors investigated were precision, effects of storage, maximum and minimum levels of quantification, face velocity effects, effects of temperature and humidity, off-gassing (related to storage), exposure to mixtures, problems associated with applicable analytical methods, and adsorption of the contaminant by the badge itself with subsequent leaching to the sensing surface. The possibility of adsorption by the badge body, thus giving

higher results if the contaminant is subsequently released to the active medium, is of special concern in using passive dosimeters to measure very low ambient concentrations such as might be found in air pollution studies. Such interest and concern are evidenced by research on the subject being sponsored by the U.S. Environmental Protection Agency (EPA).[8] Because of the lower concentrations involved with air pollution studies as opposed to workplace environments, the EPA also is concerned with the background or post-manufacture contamination levels associated with the sensing medium. Initially, the focus concerns organics and activated charcoal.

In summary, although numerous factors may affect the final calculation of concentration, only face velocity and the determination of the diffusion coefficient are unique sources of error for passive collectors. Therefore, if face velocities are sufficient to prevent "starvation" (probably greater than 7.5 cm/sec) and if diffusion coefficients have been accurately calculated or experimentally determined, passive dosimeters should give results comparable to those obtained with traditional active sampling systems.

statistical considerations

In evaluating any new monitoring method, extensive laboratory and field testing is necessary. Interpretation of the results of these tests requires the application of appropriate statistical techniques. The use of statistical techniques which are meaningful and easily understood is important; consequently, a discussion of the techniques used to evaluate passive dosimeters is appropriate.

There are numerous statistical tests which can be applied to both field and laboratory validation data. The main difference between the two situations is the degree of certainty of the "true" concentration of the monitored environment. In the field, the true value is usually an estimate based on the results of a standard sampling and analytical method. In the laboratory, experimental "known" concentrations are evolved and are then used for comparison with the concentrations estimated from sampling and analytical methods.

What is often not stated is that a certain amount of error also exists in the determination of laboratory-evolved "known" concentrations. These errors are often difficult to estimate. The "known" concentration is often calculated by weighing a syringe before and after an injection period (mass balance) or simply by injecting or allowing to diffuse a measured volume. It is assumed that the aliquot delivered was vaporized or diffused into a test chamber of known size. Possible sources of error include adsorption to or leaks from the test chamber, absorption and adsorption to articles placed in the chamber, degradation of the analyte by air oxidation or hydrolysis at high relative humidities, and error in measuring the injected contaminant. A backup monitoring system may be used to ensure close proximity to the "known" concentration. For example, an infra-red (IR) analyzer or gas chromatograph may be used as a check on a "known" concentration.

In other instances an IR analyzer or a direct reading instrument may be the only method for determining "known" concentrations. In this case the error in the instrument can be calculated or estimated. Charcoal tubes and critical orifices also have been used to measure "known" concentrations. If error in both the "known" concentration and the estimated concentration are considered, statistical tests used to validate the experimental method become considerably more complicated; hence, the error in measuring the "known" concentration is usually assumed to be small and unimportant.[9] Methods described above for determinint the "known" concentration vary in their accuracy, a fact which should be considered when evaluating validation data for any sampling and analytical method.

When one is validating a method in the laboratory, there are two main considerations: the variation of the samples or data points about their mean, and the deviation of the sample mean from the true mean or "known" concentration. The first consideration often is called precision and is probably the most important and reliable measure as it does not depend on the error in determining the "known" concentration. Precision is estimated by determining the coefficient of variation (CV) or relative standard deviation of the data set as follows:

$$CV = \frac{s}{X} \times 100 \qquad (7)$$

where: s = Standard deviation of sample data set, and

X = Mean of sample data set.

Where samples are taken at several concentrations, it is necessary to determine a pooled coefficient of variation which involves determination of number of levels tested.[10] It should be noted that determining the number of concentrations (or more appropriately, the number of statistical levels) is not always straightforward. For example, if 10 samples are taken at each of three concentrations, and if within each concentration five of the samples are collected over four hours while the other five are collected over eight hours, are there three levels or six levels? The important point to consider is whether the differentiation of a level is based upon an anticipated difference in the sample mean. Certainly if the investigator designs the experiment with different time levels, there is an anticipated effect of time on the mean. Unfortunately, when experiments are so designed, statistical analyses at the various levels usually are not performed.

The second statistical consideration, the difference between the sample mean and the "known" value, is sometimes called accuracy, but the term bias is more appropriate. It is defined as:

$$b = \frac{X - X_0}{X_0} \times 100 \qquad (8)$$

where: X = mean of sample data set, and

X_0 = "known" value at level tested.

If more than one level is sampled, it is necessary to determine the pooled bias of the data set.[11]

The bias for a given set of data can sometimes be corrected. If the average bias (either the average of several samples at one level or the pooled bias for several levels) is large, one should note if the components of the bias value (either the individual samples or the levels) are consistently negative or positive. If the bias is large and varies consistently in one direction, the precision nevertheless may be quite small. In this case a physical or chemical variable may be consistently affecting the method (a systematic as opposed to random error), causing the experimental values to constantly fall short or long of the "known" concentration. This form of bias should be corrected.

In addition to these statistical tests, others have been used to assess the validity of passive monitoring systems. Overall system accuracy[11] has been defined as (2 × CV) + absolute bias, expressed as a percent. Others[12] have used the percentage of the "known" concentration accounted for by the sample mean ± two standard deviations as well as the term systematic error[13,14] which is equivalent to overall system accuracy. Relative standard deviation has also been used, and is defined as the equivalent of CV.[15] Additionally, some authors report only raw data while others report means without standard deviations or sample sizes, and various other combinations. While all of these statistical determinations have utility, it seems important for comparative purposes to consistently use those determinations which give the most information in the simplest form. Certainly, bias and precision meet these criteria.

Discussion of one other point seems necessary. NIOSH[10] has proposed as a guideline for their own internal purposes that sampling and analytical methods meet a minimum requirement of ± 25 percent accuracy; that is, the absolute total error of the method should be less than 25 percent in at least 95 percent of the sample population (assuming a normal distribution). NIOSH derives the maximum precision value for an unbiased method given the accuracy criteria stated. This value (12.8 percent) is the maximum precision value acceptable for an unbiased method. Although the 25 percent accuracy criterion has been criticized by some authors,[16] it was adopted for NIOSH's own internal use and is not meant as public policy. However, OSHA adopted the same criterion for the benzene standard, without a complete derivation or explanation. Consequently, this criterion has been criticized and alternatives have been proposed.[17] A second important point is that bias is also considered in the ± 25 percent criterion according to a somewhat complex statistical relationship,[10] but the overall system accuracy as defined earlier[11] is a fair approximation if the method has a true bias, *i.e.*, its mean is statistically different from the "known concentration." A final point is that as the number of samples at a level increases, the standard deviation and CV should decrease. These considerations are important when evaluating passive monitor validation data, especially in those cases where manufacturers have stated that they have met the 25 percent accuracy criterion.

For field comparisons of conventional and passive monitors, different statistical tests are necessary. If passive monitor values, for example, are plotted against charcoal tube results (Y vs. X) and more than one concentration is sampled, one would expect an increase in X to cause an increase in Y. If the increase is linear, and the sample values lie on the regression line, the correlation coefficient (r) would have a value of one. If a change in X brings about an equal change in Y, then the slope would also have a value of one. If the individual values for the two devices are indeed equivalent, the line should intercept the origin. Each of these relationships is expected within reason. The difference of the slop from one, the correlation coefficient from one, and the intercept from zero can and should be tested.

In order to perform the regression analysis described above we must assume that X (active sampling data) is not subject to error. Of course, we know and can calculate under laboratory conditions the error of active sampling systems. There are at least three reasons why this error is often overlooked. First, it is assumed that consideration of the error in X would only cause small differences in regression analysis results. Second, in addition to laboratory demonstrated error, a range of errors introduced by varying environmental conditions must be considered. While difficult to assess, these errors may have a profound effect on X, and indeed the error in the X measurement may be as great or greater than that for Y. Finally, if the error in X is to be considered the statistical tests are complex. Such tests have been discussed for biological problems;[18] however, the theories apparently have not been applied to sampling and analytical methods even though their appropriateness has been recognized.[19]

applications

From a historical vantage, one of the earliest reports of a "passive" monitor for evaluation of airborne contaminants was patented by Gordon and Lowe in 1927.[20] Their gas detector for carbon monoxide involved an "easily frangible vessel containing a solution of salts including palladium chloride, and a covering for said vessel of a light colored absorbent material." The principle involved breaking the vessel (a small ampule) and noting the subsequent color change of the solution as it reacted with the carbon monoxide on the light colored absorbent material. This type of semiquantitative device was certainly a forerunner of those that are available today, though it was undoubtedly affected by air velocity as a stagnant air layer was not employed.

An extension of Gordon and Lowe's concepts in the late 1960's provided the basis for Plantz *et al.* to develop a personal dosimeter for measuring hydrazine, unsymmetrical dimethylhydrazine and monomethylhydrazine.[21] The reaction of these compounds with a "colorimetric substance" (bindone) produced a purple color, the intensity of which was dependent on both concentration and duration of exposure. Color standards then were used to estimate the concentration as a function of the time the badge was exposed to the contaminated air; consequently, the method was only semiquantitative. In considering sources of error the authors noted that the purple color would also be produced by all volatile bases that were tested, including ammonia, aliphatic amines, aniline and cigarette smoke.

Of interest in this review, however, are *quantitative* devices based on the principle of either gas or vapor diffusion or permeation through a stagnant air layer. The first such device to be reported in the literature was described by Palmes and Gunnison in 1973.[22] Their device employed the principle of gas diffusion to determine airborne concentrations of sulfur dioxide and will receive further consideration subsequently. To gain the best overview of the various applications of these concepts, it is probably best to proceed by considering first the inorganic and then organic gases and vapors.

inorganic gases and vapors

ammonia

In 1978, Mazur *et al.* described the use of the Abcor GASBADGE to sample employee exposure to ammonia (this device currently is not marketed).[24] The investigators replaced the charcoal pad normally found in the GASBADGE with an acid impregnated absorption pad. Of three acids tested, phosphoric was most successful in providing the best approximation of theoretical concentrations. They determined, however, that volatile amines, specifically cyclohexylamine, could produce high readings, as high as 185 percent of the synthetic atmosphere. This led them to replace the glass fiber draft shield on the front of the GASBADGE with a "charcoal impregnated glass fiber filter which had been pretreated with alcoholic KOH containing 0.1 percent surfactant." The charcoal served to adsorb amines as they diffused into the dosimeter, while the KOH (aided by the wetting agent) eliminated irreversible ammonia adsorption on the charcoal, which would have caused underestimation of the ambient concentration. Additional laboratory experiments demonstrated that storage time of up to 47 days, prior to analysis, did not appear to adversely affect the results.

More recently, DuPont has developed a commercially available system for the measurement of several airborne contaminants including ammonia. In 1981, Kring *et al.* described DuPont's PRO-TEK™ system for ammonia, nitrogen dioxide and sulfur dioxide sampling analysis using a colorimetric readout instrument.[23] The ammonia badge relies on molecular diffusion of ammonia and subsequent chemical reaction with a solution of 0.3N boric acid and 0.03N sodium potassium tartarate (*sic*). After exposure, the reagent pack is removed from the badge holder and analysis is initiated by pressing reagent "blisters" which are adjacent to the absorbing solution. This action causes the release of a modified Nessler's reagent and the subsequent development of a colored solution. For ammonia, maximum color intensity is developed at 425 nanometers. The absorbance of the sample is then compared against a standard curve based on Beer's Law. After determination of the precision of the analytical method and verification of the linear range of the color chemistry, laboratory testing was conducted to establish the operational range as well as precision and accuracy of the overall method (see Table I). The minumum and maximum limits of the sampling range were found to be 50 and 500 ppm-hours, respectively. For an eight-hour time weighted average, these values correspond to one-fourth and two and one-half times the current ACGIH Threshold Limit Value of 25 parts per million.[25] In considering sources of error, environmental effects including temperature (10 to 40 °C), relative humidity (10 to 80 percent), pressure (730 to 790 mm Hg), and face velocity (2.5 to 125 cm/sec) were included. Of the environmental factors evaluated, temperature and the concentration of the contaminant were identified as being responsible for 98 percent of the data variation. For ammonia, a temperature correction factor of 0.6 percent per degree centigrade was suggested. Also investigated was the storage stability of both unexposed and exposed badges. Results indicated that refrigerated storage is necessary to extend the shelf life of unexposed badges. Once the badge is exposed to ammonia and before the reagents are mixed, the badges can be stored for one (room temperature) to three (refrigerated) weeks without losing any absorbed contaminant. Once the reagents are mixed and color formation is started, the badge should be read within 90 minutes. Additional testing results conducted by DuPont are shown in Table I.[26]

carbon monoxide

Shor and Anders, of the 3M Company, have described the 3M "direct-read diffusional monitor" for evaluation of exposures to carbon monoxide.[27] The principle involves the reaction of the carbon monoxide and an unreported reagent(s) to give a visible color change from pink to tan. Theoretically, "if any pink color is observable at the end of the exposure period, then the exposure was less than the one time-weighted-average of 400 ppm-hours." They also state that noting the time to the endpoint allows for calculation of the average concentration of carbon monoxide during the exposure period. The authors present summary results of laboratory evaluations using an infrared radiation device to establish "known" concentrations (see Table I).

chlorine

Hardy *et al.* have described a personal chlorine monitor (REAL, Inc.) which employs the principle of permeation of the gaseous contaminant through a silicone membrane and into 10 mL of a fluorescein-bromide solution.[28] Colorimetric techniques then can be applied to determine the chlorine concentration. The authors report a detection limit of 0.013 ppm chlorine for an eight-hour exposure, with a "working range" of 0.1 to 2.0 ppm. They also suggest that for shorter time periods, concentrations of up to five ppm can be determined. Other observations included effects of temperature, humidity, absorbent concentration, pH and response time, with all laboratory results presented graphically.

Moleculon Research Corporation has recently introduced a chlorine monitoring device which relies on plastic film impregnated with liquid reagents.[29] Exposure of the badge to chlorine gas gives a visible, "blue-purple," color change. Optical transmission measurements, and comparison with a standard curve, can then provide quantitative exposures in ppm-hours. The manufacturer's summary results indicating effects of temperature, humidity, wind velocity and concentration are reported as presenting an error at the 95 percent confidence level, which is "less than ± 15 percent."

TABLE I
Inorganic Gases and Vapors Laboratory Results

Chemical	Dosimeter[A]	Bias[B]	Precisi n[C]	Range[D] (ppm)	Reference	Notes
Ammonia	DP	0.5	7.4	20-50	24	
	DP	0.5	6.9	20-48	26	
	GB	−3.2	9.3	6-62	23	EG
Nitrogen	GB		21.7	4-11	1	HI
Dioxide	DP	−3.2	7.5	4-11	38	
	DP	−0.9	8.7	4-11	24	
	MDA	−4.9	4.1	6-9	36	EG
Sulfur	GB		13.8	4.6-5.3	1	HI
Dioxide	DP	−1	5.8	4-11	38	
	DP	−0.8	7.5	4-11	24	
Hydrogen Sulfide	GB		15.3	1.6-2.2	1	HI
Mercury	3M	0.5	9	0.03-0.3mg/m³	32	F
	3M	17	2	0.05-0.2mg/m³	33	EG
CO	3M	0.3	4.7	50-1830	27	G

[A]DP=DuPont Pro-Tek Colorimetric System Badges. 3M=3M Company Monitor, MDA=MDA Scientific, GB=Abcor GASBADGE

[B]See text, equation (8)

[C]See text, equation (7)

[D]Some values are rounded to nearest whole number

[E]Bias consistently negative

[F]Results derived from Table III of McCammon *et al.*[32]

[G]Results calculated from data provided in reference

[H]This product is not currently marketed

[I]Bias could not be calculated from data given

hydrogen sulfide

In 1977, Tompkins and Goldsmith described the development of the GASBADGE personal sampler.[1] Although later work with this device focused on the collection of organics on an activated charcoal substrate, initial studies researched sampling of both organic and inorganic compounds. (The GASBADGE for organic vapors is now marketed by National Mine Safety Company, and those for inorganic vapors are not currently marketed.) Applications involving inorganic gases relied on collective elements of an "appropriate substrate impregnated with a chemical medium specific for the contaminant of interest." Based on 60 observations, the authors' statistical summary is presented in Table I. Eighty percent of the measurements were within ± 25 percent of the "true" value. Challenge concentrations were established in a "well-mixed" environmental test chamber and were measured with an "independent wet-chemistry sampling train."

Hardy and associates have described a permeation device (REAL, Inc.) which relies on the permeation of H_2S through a dimethyl silicone membrane and subsequent reaction with a solution of 0.2N sodium hydroxide and EDTA.[30] The colored product (methylene blue) is measured spectrophotometrically and compared with a calibration curve to determine ppm-hours. A knowledge of exposure time then allows for the determination of average exposure over the measurement period. The authors note that a critical step in the development of such a device is the experimental determination of the permeation constant (see Equation 6), which involves calibration of each monitor by exposure to known concentrations of the contaminant. The results of this laboratory research demonstrated a detection limit of 0.01 ppm for an eight-hour exposure, with a working range of 0.1 to 20 ppm and a linear response up to 200 ppm. The working range corresponds to one one-hundredth to two times the current eight-hour TLV of 10 ppm.[25] Evaluations of environmental effects indicated that neither temperature, over the range of −3 to 39 °C, nor humidity, from 0 to 99 percent relative, caused any significant variations in response of the device. Further research demonstrated a good response to high concentrations in less than one minute, adequate sample stability up to 10 days if EDTA is used in the absorbing solution, and negative and positive interferences, respectively, from chlorine gas and nitrogen dioxide. Precision and bias were not reported.

Another approach for the determination of gaseous hydrogen sulfide has been reported by Graedel and Franey.[31] Their research involved using a semiquantitative method without a stagnant air layer and relying on the discoloration of lead-stabilized polyvinyl chloride (PVC). The technique involves the diffusion of gas in a polymer and, at high H_2S levels, the detection rather than the measurement of toxic levels of H_2S. Screening applications for low level exposures also are discussed.

mercury

In 1977, McCammon and Woodfin of NIOSH reported the results of a laboratory evaluation of 3M's mercury vapor monitor.[32] The monitor's operating principle involves molecular diffusion and deposition of mercury vapor on a gold substrate. The resulting change in electrical conductivity across the gold foil is related to the amount of mercury absorbed by the foil. Three other sampling methods, all of which involved the active movement of air, also were investigated and include the LASL tandum sampling tube, the hopcalite tube, and the iodine impregnated charcoal tube. For the passive monitor, precision and accuracy, the effects of face velocity and temperature, and potential interferences were investigated. Concentrations of mercury vapor in an exposure chamber were monitored with an ultraviolet mercury vapor meter, which in turn was calibrated by measurements using the LASL method. To determine precision of the monitors, 12 devices were exposed to a test atmosphere. Results from three measurements of the test atmosphere using the LASL method gave an "expected" concentration of 0.056 milligrams of mercury per cubic meter of air (mg m^3), with a standard deviation (SD) of 0.002 mg m^3 and a coefficient of variation (CV) of 0.037. Precision and bias calculated for the data given in Table III of McCammon *et al.*[32] is summarized in Table I. A least squares regression analysis of the combined precision and accuracy results for the passive dosimeters versus the "known" concentrations gave a Y intercept of −0.004 mg m^3 and a slope of 1.003. Tests for the effects of face velocities from 25 to 125 cm sec (50 to 250 fpm) did not appear to have any adverse effect on performance, while variation of temperature experimentally confirmed its effect on both the diffusion constant and the concentration of the contaminant. The potential effects of changes in relative humidity were not discussed by the authors. The other area of investigation in this study involved potential interferences of chlorine, sulfur dioxide, and hydrogen sulfide. Concomitant and sequential exposure to mercury and chlorine, the latter at high levels (5.8 ppm), produced a negative bias, but a similar effect was observed with the UV meter and the LASL system. The authors suggested that the mercury and chlorine may have been reacting to form mercuric chloride which was not being measured by any of the systems. The interference effects of sulfur dioxide and hydrogen sulfide, although less than chlorine, also were confirmed.

In 1980, McCammon and his NIOSH and OSHA coworkers conducted further tests of the four previously described mercury vapor sampling and analytical methods.[33] The design of this laboratory experiment involved intercomparison of four methods, and the findings suggested that the variability of the iodine charcoal tube method is significantly different from that of the other three methods. It was observed that the other three methods, including the 3M passive dosimeter, exhibited good precision over the concentration range of 0.05 to 0.2 mg m^3 as shown in Table I.

Recently SKC, Inc., introduced a gas monitoring badge (produced by GMD, Inc.) which uses the principle of molecular diffusion (without a stagnant air layer) to collect mercury vapor.[34] The sampling media is referred to as "Hydrar Sorbent," and "extensive" but unpublished field and laboratory testing are cited to show that "chlorine, moisture, etc., do not interfere" with measurements. HYDRAR is developed from a "manganese dioxide catalyst material similar to 'Hopcalite.' " Quantitative determination is made by chemical desorption of the mercury and analysis with atomic absorption.

nitrogen dioxide

In 1976, Palmes *et al.* reported the results of their evaluation of a personal sampler for nitrogen dioxide (NO_2).[35] This work was an extension of their earlier pioneering efforts in developing a personal sampler, employing the principle of gas diffusion, for sulfur dioxide.[22] In their design, the sampling device was a 1.3 cm (0.5 inches) acrylic tube, 7.1 cm (2.8 inches) long. At the "closed" end of the diffusion path (tube) were placed three stainless steel grids coated with triethanolamine (TEA). TEA was selected because: 1) it captures NO_2 efficiently, 2) it provides a stable sampling surface, and 3) it yields a chemical complex with NO_2 that is very stable over time. Subsequent analysis yielded a colored complex whose absorption was measured at 540 nanometers. Results were then compared against a standard curve which obeyed Beer's Law. The experimental evaluation of the NO_2 sampler involved chamber measurements compared with "known" values determined by the volume of NO_2 introduced to the chamber or the weight loss of NO_2 from a permeation tube. Although neither individual nor summary results were presented, graphical comparison of the data indicated a close agreement between the passive sampler results and theoretical concentrations. The effects of wind velocity and direction as well as stability over time also were considered. In determining wind effects, the uptake of water vapor, rather than NO_2, was measured. The results indicated that there was an increase in average uptake with increased velocity and that the 45 degree incident angle gave the highest uptake (135 percent at 258 cm sec). Across all angles of exposure (0 to 180 degrees) the average uptake increased from 2 to 14 percent as the wind velocity increased from 50 to 258 cm sec (100 to 516 fpm). Stability studies indicated that the badges could be used for months both after preparation and before exposure as well as after exposure and before analysis.

In the previously described studies with the GASBADGE, Tompkins and Goldsmith also monitored for nitrogen dioxide.[1] Their summary results for 82 observations showed accuracies and precisions as summarized in Table I. Eighty-five percent of the observations were within ± 25 percent of the "true" value.

A commercial model of the Palmes passive sampler has been marketed by MDA Scientific, Inc., and additional laboratory testing demonstrated a linear collection efficiency for any given dose, *i.e.*, concentration × time (see Table I).[36] The sampler exhibited a consistently negative bias as compared to concentration determinations using a continuous monitor and the NIOSH wet chemical method.

As noted earlier, the DuPont PRO-TEK system includes a badge for nitrogen dioxide. Laboratory test results of this device are shown in Table I.[37]

sulfur dioxide

As noted previously, pioneering work in 1973 on the design of a sampling device which relies solely on diffusion of gaseous contaminants through a stagnant air layer is attributed to *Palmes and Gunnison.*[22] *Their initial studies* involved experimental work on different tube lengths. The collecting medium was a complex of mercuric chloride and the final analysis involved colorimetric determination. The studies demonstrated that, except for very short diffusion paths (tube lengths), the diffusion monitor satisfactorily duplicated the results obtained by both wet chemical and conductrimetric measurements. Although this study did not go into the ramifications of environmental effects and interferences, it should be recognized as an important step in developing a new industrial hygiene technology.

The last of the three inorganic gases looked at by Tompkins and Goldsmith in their studies of the GASBADGE was sulfur dioxide.[1] Summary data for 23 observations on this gas are included in Table I. One hundred percent of the observations were within ± 25 percent of the "true" values.

The results from DuPont's tests on their sulfur dioxide badge also are shown in Table I.[38]

organic gases and vapors

Most passive dosimeters designed to sample for organic gases and vapors use activated charcoal as the adsorbing medium. As we know from its extensive use in active systems, activated charcoal has an affinity for a wide range of organic compounds. Consequently, the discussion on the applications of passive dosimeters for the measurement of organic gases and vapors first will focus on devices using activated charcoal and then will turn to specific organics which rely on other collecting media.

TABLE II
Organic Gases and Vapors Laboratory Results

Chemical	Dosimeter[A]	Bias[B]	Precision[C]	Range[D] (ppm)	Reference	Notes
Carbon Tetrachloride	DPA	0.4	4.4	3-18	10	E
Toluene	DPA	0.3	5.25	57-228	45	
	NMS	−1.7	1.7	12-47	13	F,J
Formaldehyde	DP	1.5	6.3	0.2-4.2	55	
Benzene	DPB	3.3	4.7	3-24	46	
	NMS	−4 1	1.7	0.8-5.4	13	F,J
	NMS	1.8	17	13-13.5	1	E,G,J
Ethylene Oxide	3M	−1.4	3.2	300	53	J
Halothane	3M	3	7.4	0.5-20	44	J
Enflurane	3M	−2.8	4.8	0.5-20	44	J
Acrylonitrile	NMS	0 03	8.7	0.7-19	39	
Hexane	NMS	−1.2	2	10-37	13	F,J
Vinyl Chloride	R	−0.2	3.7	1.5-14	2	H,J
Methyl Chloroform	3M	−5.9	4.7	160-840	48	I,J
	DPA	−10.6	4.5	160-840	48	E,I,J
	NMS	2.4	2	15-65	12	F,J
Trichloro-ethylene	3M	−3.9	7.6	20-200	48	I,J
	DPA	−6.9	7.7	20-200	48	E,I,J
	NMS	−0.5	1.9	15-67	12	F,J

[A]3M = 3M Company Organic Vapor Monitor, DPA and DPB = DuPont PRO-TEK G-AA and G-BB Organic Vapor Badges, NMS = National Mine Safety GASBADGE, R = Real, Inc. MINIMONITOR, DP = DuPont PRO-TEK System Colorimetric Badges

[B]See text, equation (8)

[C]See text, equation (7)

[D]Some values are rounded to nearest whole number

[E]Small sample size

[F]Knowns were calculated using charcoal tubes with critical orifices. This could affect the bias measure

[G]Preliminary results

[H]Permeation dosimeter

[I]Bias consistently negative

[J]Results calculated from data provided in reference

·tivated charcoal devices

s of March, 1982, there were four manufacturers of passive simeters which rely on diffusion and subsequent adsorpn on to activated charcoal: National Mine Service Comny (GASBADGE), 3M Company (Organic Vapor Moni-), DuPont Company (PRO-TEK, G-AA and G-BB ganic Vapor Air Monitoring Badge), and the Mine Safety pliance Company (Vaporgard Badge).

In 1977, Tompkins and Goldsmith described the first mmercial passive dosimeter for monitoring organic pors.[1] The GASBADGE relied on molecular diffusion of vapor into the badge and subsequent adsorption onto tivated charcoal. The authors developed the theoretical rinciples of the badge's operation, and discussed sensitivity temperature and pressure, face velocity effects, and sponse time. Preliminary results showing the badge's sponse to benzene, ethyl acetate, methyl ethyl ketone, and yrene also were presented and were described as "very couraging" (see Table II).

In the same year, Silverstein reported results of laboratory d field testing of the GASBADGE for acrylonitrile.[89] The sults of the exposure of 33 badges to known concentraons in the laboratory are presented in Table II. The results dicate the acceptability of the GASBADGE for measureents of acrylonitrile over the range of 0.75 to 19 ppm. The ne of exposure in the laboratory was not given, however, eld measurements did cover periods of up to seven hours. Though temperature and relative humidity ranges were ported, data analysis to determine the effects of these riables was not presented. Silverstein also looked at sorption efficiencies and determined that the best results [redacted]rcent) were obtained with four mL of two percent etone in carbon disulfide.

In 1978, Bamberger *et al.* conducted a series of laboratory sts to evaluate the GASBADGE.[12] Their approach involved e generation of known concentrations of solvents and bsequent evaluation with charcoal tubes (active sampling) nd the passive dosimeter. To evaluate the applicability of he dosimeter over a wide range of compounds, the investiation included seven different organic compounds each presentative of a different functional group. Included in his study were: benzene (aromatic), n-butanol (alcohol), -butyl acetate (ester), isooctane (alkane), methyl chloroorm (halogenated alkane), methyl isobutyl ketone (ketone), id trichloroethylene (halogenated alkene). The diffusion efficient (D) used was that supplied by the badge manufacrer, except in the case of isooctane which was reported as ing an unknown coefficient. Computations involving is compound relied on the coefficient for n-octane. A variety of experiments was conducted to look at a wide range of questions. Their findings corroborated dosimeter conerns similar to those of active systems using charcoal tubes, e.g., minimum and maximum loadings are important, postmple contamination and loss can occur if the exposed bsorbent is not adequately sealed, percent recovery for ixtures is consistent with percent recoveries for single [redacted]ounds, and differences in charcoal lots can give differnt results. Other tests confirmed the need for some air movement across the badge face and the lack of effect of temperature changes over a small range (11 °C). The results of the simultaneous sampling with the badges and the charcoal tubes indicated that the badges had a consistent negative bias. The authors suggested that, because the results were so reproducible, corrections for adsorption desorption efficiencies less than 100 percent can be accomplished just as is done for charcoal tube data.

In 1979, Hirayama and Ikeda evaluated the application of the GASBADGE for monitoring exposures to mixed solvents.[10] Their research involved different preparations of activated carbon "felt" in place of the supplied collection medium and exposure to mixtures of n-hexane, ethyl acetate and toluene. Summary (graphical) data indicated that the amounts of contaminant absorbed by the dosimeter were proportional to both the vapor concentrations and time of exposure.

Halliday and Anderson reported on the use of the GASBADGE in monitoring for halothane.[11] Six observations indicated a range of measurements from minus nine to plus ten percent of the test atmospheres. Unfortunately, the authors did not report their procedure for determining the concentration of halothane in the test atmospheres.

In 1981, Evans and Horstman reported evaluations of desorption efficiencies of charcoal tubes and the GASBADGE for styrene.[12] For liquid dosing they found the dosimeter to be similar to the tube, while for vapor dosing the badge was superior. The authors suggested that the differences in results may have been related to the use of coconut shell carbon in the tubes and petroleum derived carbon in the badge. They did not explain why this difference would affect one method of dosing and not the other.

In 1980, Anders and Mullins of the 3M Company presented results comparing the 3M passive monitor with charcoal tubes in sampling for mixtures of organic compounds.[13] The laboratory tests included a binary mixture of toluene and methyl ethyl ketone; a tertiary mixture of benzene, toluene and xylene; and complex mixtures of unleaded and leaded gasoline containing various alcohols. Although the investigators cited "excellent" precision and accuracy for the diffusional monitor, sample sizes were small, and the complicated study design and lack of raw data preclude the determination of precision and bias statistics.

Mazur and his co-workers[14] conducted side-by-side laboratory and field tests with charcoal tubes and 3M organic vapor monitors to measure concentrations of halothane (2-bromo-2-chloro-1,1,1-trifluoroethane) and enflurane (2-chloro-1,1,2-trifluoroethyl difluoromethyl ether). The results of the laboratory studies are presented in Table II and support the authors' conclusions that the dosimeters are a reliable method for the collection of enflurane and halothane.

In 1980, Lautenberger *et al.* described DuPont's passive monitor for organic vapors.[15] Each charcoal strip in the PRO-TEK G-AA Organic Vapor Badge contains approximately 300 mg of coconut-based activated charcoal impregnated in an inert polymer. A dual sampling rate of approxi-

mately 50 or 100 ml · min is determined by the removal of one or both of the dosimeter's protective covers. One aspect of their research involved experimental determination of the diffusion coefficient of several gases and vapors. They reported that values calculated by Fuggi[15] were within 10 percent of their experimentally determined diffusion coefficient values. Preliminary experimental results were used to discuss face velocity effects, range and sensitivity, maximum and minimum sampling times, vapor retention, storage stability, desorption efficiency, and overall badge efficiency. The overall accuracy determinations were limited to four observations at each of two concentrations of carbon tetrachloride (see Table II). However, the presentation of raw data, as well as an explanation of the statistical tests applied, is most useful. This same detail of information is also found in DuPont's validation reports for toluene and benzene (see Table II).[15,16]

In the benzene report, DuPont also describes its PRO-TEK G-BB badge. This badge has a backup section of charcoal, which serves the same purpose as the second section in a charcoal tube, *i.e.*, to aid in determining if the sampler has been overloaded. The 3M Company also markets an Organic Vapor Monitor with a backup section.[17]

In studies of the measurement of waste anesthetic gases with passive dosimeters, Jonas *et al.* evaluated the GASBADGE, 3M Organic Vapor Monitor and DuPont Pro-Tek in measuring enflurane.[6] Unfortunately, the badges were not identified in the presentation of the results although interpretation of the reported sampler geometry would indicate that A was the DuPont badge, B was the 3M badge, and C was the GASBADGE. The results of their laboratory studies indicated that badge B had the lowest coefficients of variation (CV was not calculated as described in this text) as compared to concentrations determined by infrared analysis. Badge A had a low CV (9 percent) at 5 ppm and a much higher value (CV=34 percent) at 20 ppm. The C badge had consistently high CV's ranging from 23 to 30 percent. It should also be noted that the charcoal tube CV's ranged from 11 to 27 percent, that desorption efficiencies for the badges ranged from 0.81 to 1.17, and that IR analyses of tank concentrations were constantly lower than expected. If badge B was the 3M device, the results of Jonas *et al.* support those reported by Mazur *et al.*[14] Further testing of badges A and C seems necessary, however, to confirm their seemingly low precisions.

Mazur and his coworkers conducted additional tests comparing the 3M and DuPont badges against charcoal tubes.[18] Methyl chloroform and trichloroethylene, two solvents widely used in vapor degreasing operations, were sampled. In the laboratory phase of the study, the badges and charcoal tubes were exposed to chamber concentrations over the range of 160 to 840 ppm of methyl chloroform and from 20 to 200 ppm of trichloroethylene. Exposure times varied from two to six hours for methyl chloroform and from four to six hours for trichloroethylene. The laboratory work indicated that the percent recoveries of the various doses (concentration × time) were in good agreement except for one exposure of the 3M badge which involved a five hour exposure at 700 ppm. The authors noted that this exposu of 3500 ppm-hours exceeded the upper exposure limit pr vided by the manufacturer. The overall mean recovery valu for each type of sampler was used to correct all subseque field data. In addition to the recovery measurements, th laboratory phase of this study also involved determinatio of storage stability. The authors found no significant loss of methylchloroform or trichloroethylene from either badg following storage of exposed badges for up to three week

In 1978, West and Reiszner reported on the field tests o the MINIMONITOR™ (REAL, Inc.) permeation person monitor for vinyl chloride.[2] This monitor was a modific version of one previously described by Nelms *et al.*[19] Th collecting medium was activated charcoal, but rather tha relying on molecular diffusion, the badge design involved polymeric membrane and the permeation of vinyl chlorid through the membrane and adsorption onto the charcoa Initial laboratory calibration was used to determine th permeation constant of the device. Laboratory results ind cated good accuracies as summarized in Table II.

During the same period that Tompkins and Goldsmith were describing the GASBADGE, Bailey and Hollingdale Smith of Great Britain were presenting their ideas for a personal passive sampler for organic gases and vapors.[20] Their design involved the use of either one of two types o membrane and subsequent adsorption onto activated char coal. They found two membranes to be satisfactory, one o thin silicone rubber which acted as a permeation barrier, an the second a porous polypropylene film which allowed fo molecular diffusion of the gas and vapor. They conducte laboratory tests using carbon tetrachloride, styrene an dichlorodifluormethane. Their test results do mix some ter minology, *e.g.*, permeation rates for both the permeatio device and the diffusional device, but did provide an earl demonstration of the feasibility of such a device for monitor ing certain organics. The device, the Porton Diffusion Sampler, seems to see its greatest use in Great Britain.

acrylonitrile

One of the newest applications of passive dosimetry involves the use of a porous polymer (Porapak® N) as the collecting surface with subsequent thermal desorption and gas chromatographic analysis. Benson and Boyce have described such a device and its utility in sampling for acrylonitrile.[21] Laboratory testing for acrylonitrile involved comparison of the dosimeter values with concentrations measured on a gas chromatograph. Initial experimentation indicated that the dosimeter can be used for acrylonitrile concentrations in the range of 4 ppm, but at concentrations of 2 ppm a 40 percent error is reported.

aniline

In addition to activated charcoal, another widely used adsorbent medium is silica gel. To study the utility of this material, Campbell and Konzen constructed passive dosimeters from glass culture tubes (1.05 cm inside diameter) with 40 60 mesh silica gel as the collecting surface.[52] Laboratory testing involved exposure of the dosimeter to aniline, with exposure concentrations determined by gas chromatographic analysis of ethanol gas scrubbers. Three different

size (length) dosimeters were evaluated, with the best results obtained with the intermediate length tube (L = 3.0 cm; A L = 0.3 cm). The authors present raw data and clearly described their statistical techniques.

[redacted]ylene oxide

Wallins and Anders have recently described the 3M diffusional monitor for sampling ethylene oxide in air.[53] In this badge the collecting surface is described as a "chemically impregnated charcoal surface, (where) a reaction occurs producing a stable compound with a vapor pressure substantially lower than the parent compound." The authors present statistically summarized data describing the linearity and capacity of the monitor, the recovery of absorbed ethylene oxide, environmental effects, sample stability, and the effects of potential interferences. Precision and bias are presented in Table II.

formaldehyde

Rodriguez *et al.* have described another 3M diffusional monitor for sampling formaldehyde.[54] In this diffusional monitor, the collecting surface is an "impregnated sorbent" which can then be desorbed *in situ* with water and the concentration of formaldehyde determined colorimetrically. Laboratory evaluation first involved determination of recovery coefficients, which at eight ppm-hours (19.5 micrograms) were found to be 1.00 ± 0.04 over six tests. The next step involved determination of the dosimeter's "sampling rate" (DA/Δt) by exposing the dosimeters to "known" concentrations of formaldehyde as generated by a permeation tube. The effect of relative humidity on the sampling rate [redacted] was investigated, and evaluation of the data did not indicate any statistically significant differences between the rates at 50 and 85 percent relative humidity. The study protocol then involved simultaneous exposures of impingers (modified chromotropic acid method) and dosimeters. The authors concluded that "the measured values by both methods lie within ± 25 percent of the expected response" and that "less variation is observed in the monitors than in the impingers." However, neither precision nor bias were reported. The authors also investigated effects of storage and determined that at elevated temperatures (38 °C) losses up to 11 percent occurred after one week, however no significant loss was seen for samples stored at 23 °C. The authors briefly discussed the potential for a negative interference from phenol and described the use of modified calibration curves to address this problem.

DuPont's PRO-TEK series of colorimetric Air Monitoring Badges, includes a badge for formaldehyde. The collection principle involves a chromotropic acid-sulfuric acid reaction. Laboratory evaluation (42 samples) of the device at seven exposure levels revealed results as shown in Table II.[55] Additional studies also were conducted on temperature and storage effects. The raw data and statistical analysis procedures are presented.

Kriesel[56] has described a new passive dosimeter for formaldehyde which is a modified version of the Palmes tube. [redacted] the present time experimental data concerning this device are not available.

phosgene

Matherne *et al.* have recently described the GMD, Inc "passive dosimeter" which provides a semiquantitative measurement of phosgene exposure.[57] The badge involves direct contact between the contaminated air and a chemically impregnated tape and therefore does not rely on a stagnant air layer. The treated paper stain intensity is reported to be logarithmically proportional to the phosgene dose over a range of 2 to 100 ppm-minutes. For quantitative measurements the badges can be read colorimetrically.

other methods

Hill and Fraser have described the use of commercial detector tubes modified to act as passive dosimeters.[58] In their research, common length-of-stain detector tubes were modified by cutting off the conical end of the tube and removing some of the indicator column material. This leaves an orifice with a cross-sectional area equal to that of the inside of the tube and a path length determined by the distance from the end of the tube, to the beginning of the indicator material. One would expect, however, that as the sorbent material becomes exposed, *i.e.*, the length of stain increases, the diffusion path length will also increase, thereby changing the sampling rate. Their evaluation of these devices involved separate laboratory exposures to toluene, ethanol and isopropanol. The results of their work, although presented only in graphical summary, demonstrate the potential for the use of modified commercial detector tubes as passive dosimeters.

field validation

Relatively few studies have been published in which passive dosimeters have been compared side by side with charcoal tubes or other conventional sampling methods under actual field conditions. For inorganic compounds only two studies, involving nitrogen dioxide[59] and chlorine,[60] have been identified. For organic compounds, eight studies[2,9,39,44,45,51,60,61] have involved field comparisons, with the number of compounds per study ranging from one to 22. In three of these studies, statistical analyses of data were not presented and cannot be performed because of small sample size or insufficient presentation of data.

Jones *et al.*[59] conducted a field evaluation for NO_2 in a salt mine, which contained diesel equipment as the NO_2 source. At each of 16 different fixed area locations, two Palmes dosimeters and two TEA tubes with pumps were used to sample the atmosphere. The active sampling (pump) method gave a coefficient of variation (CV) of 8.7 percent while for passive tubes the CV was 5.8 percent. Regression analysis (where the active system was the X variable) of their data gives a correlation coefficient of 0.69, a slope of 0.59, and an intercept of 2.05 ppm for data over the range of 3.7 to 5.5 ppm as sampled by the active method. This indicates that the dosimeter gave consistently higher readings which is reflected in the means for the two methods: 4.51 ppm for passive and 4.14 ppm for active sampling. The authors did not report wind velocities, but low velocities, as would be expected with area samples, should have caused passive

values to be low as compared to active values; this was not the case. On the other hand, high face velocities could have led to the observed positive (passive versus active) bias.

Hardy *et al.*[28] reported the raw data results from a field evaluation of a permeation chlorine monitor (REAL, Inc.). Thirteen comparisons were made in which the results from a battery operated pump and an impinger sampler were compared with the measurements from either two or three permeation samplers. To further evaluate their results, the investigators performed a regression analysis using their permeation sample means for each comparison as the dependent variable. The results are quite good with a correlation coefficient of 0.95, a regression slope of 0.85, and an intercept of 0.15 over a range of 0.03 to 1.1 ppm as detected by the impinger. It should be noted that with five impinger samples of less than 0.1 ppm, the corresponding permeation devices detected considerably higher concentrations (0.16 to 0.4 ppm).

Silverstein[39] reported field results for acrylonitrile monitoring using 18 paired samples of GASBADGE passive monitors and active systems (charcoal tubes and pumps) over a range of 0.8 to 3.8 ppm as determined by the active method. The differences in results using the active system as a reference ranged from −0.7 to 1.5 ppm. The difference in means, 2.18 for the passive versus 2.73 for the active system, was 25 percent. Further data were not presented.

West and Reiszner reported five sets of field results for vinyl chloride sampled with permeation dosimeters (REAL, Inc.) and charcoal tubes.[2] Further interpretation of their results is presented in Table III. In each case data for the active system are the X values. Four of the correlation coefficient values are very near one, reflecting good correlation, however, the slopes show quite a large degree of variability (0.69 to 1.31), indicating that badge values may fall either well below or above charcoal tube values. In those cases where the slopes were less than 1.0, very high humidities (67 to 91 percent) were reported by the authors. This factor may have interfered with permeation, although the authors reported that humidity had no effect in laboratory validations; hence the variation in slope remains unexplained. The authors noted that the overall field results showed that the badges had a slight positive bias.

Hickey and Bishop exposed 78 pairs of side-by-side charcoal tubes and 3M Organic Vapor Monitors to complex mixtures of organic chemicals in tire manufacturing operations.[9] Generally the sampling period ranged from three to five hours, and most observations consisted of one monitor and the time weighted average concentration from two sequentially exposed charcoal tubes. Sixty-four of the sets were personal samples, while the remaining 14 were area samples. The samples were collected in two separate plants (30 sample pairs in one plant and 48 in the other). Of the 22 organics potentially available for analysis, 10 were detected over a sufficiently wide range of concentrations to allow for appropriate statistical analysis by linear regression. The results are interesting in that in the first plant, 9 of the 10 organics measured by the dosimeters showed higher vapor concentrations as compared to the charcoal tubes, while in the second plant only three substances had a regression slope greater than one. The combined data for both plants did not indicate that the passive system was consistently biased when compared to the active system. The authors did point out that generally the Y-intercepts (Y=passive dosimeter data) were slightly negative, a finding which may indicate a lack of sensitivity on the part of the dosimeters at low concentrations. For the remaining 12 compounds, paired t-tests revealed no significant difference between the charcoal tube and passive monitor means at the 95 percent confidence level. The use of t-tests to analyze such data has been questioned since the means of the two methods may be very similar but the components of paired values can be considerably different.[19] This condition can only be revealed through regression analyses.

TABLE III
Regression Analysis of Vinyl Chloride Field Data[2]

N	Range (ppm)	r	Slope	Y-Intercept
7	0.02-1	0.99	1.19	0.03
8	0.08-1.8	0.99	0.69	0.05
12	0.02-6.9	1.0	1.31	0.01
39	0.05-1.8	0.82	0.81	0.11
24	1.48-16.7	0.96	1.08	0.43

In 1980, Mazur *et al.*[44] reported limited field data for halothane and enflurane measurements using both 3M Organic Vapor Monitors (OVM) and an active system (charcoal tubes and pumps). For halothane three paired samples were reported. The mean concentration for the active system was 2.01 ppm while 1.9 ppm was reported for the OVM, a difference (relative to the active system) of five percent. Only one data pair was reported for enflurane: 0.49 ppm for the OVM and 0.52 ppm for the active system. Obviously, more data are needed to draw conclusions regarding a comparison of the two methods for these agents.

A second study by Mazur *et al.*[48] reported field comparisons of passive dosimeters and active systems (pumps and charcoal tubes) in sampling for trichloroethylene (TCE) and methylchloroform (MC). Both DuPont PRO-TEK and 3M Organic Vapor Monitors were used for the passive systems. Personal samples included exposure of one each of all three monitors. Area sample results involved three average values, one was the average of three charcoal tubes, and the other two, the average of two of each type of dosimeter. For MC 11 personal and 7 area data points collected over time periods of 1 to 5 hours at 15 to 21 °C and 35 to 40 percent relative humidity were reported. For TCE, 22 personal and 7 area data points collected over periods of about 1 to 6 hours at 18 to 24 °C and 30 percent relative humidity were reported. A regression analysis in which the charcoal tubes were the independent variable was reported by the authors. In each of the following data sets the presented values involve TCE personal and stationary sampling followed by MC personal and stationary sampling. For the DuPont badge, regression

slopes of 1.0, 0.99, 0.99, and 0.98, and correlation coefficients of 0.98, 0.98, 0.94, and 0.94 were obtained. For the 3M badge, regression slopes of 1.08, 1.06, 1.07, and 0.90, and correlation coefficients of 0.98, 0.98, 0.98, and 0.90 were determined. These values appear to be quite good; however, the authors did not report if they tested the statistical significance of these values. They also did not report average of face velocities associated with stationary samples.

Evans *et al.*[60] of Great Britain reported field validation data for the Porton diffusion device while measuring methyl ethyl ketone. In this case the conventional sampler was a pump and a cassette fitted with a charcoal cloth similar to that used in the Porton device. A regression analysis performed with their data showed good correlation (0.9) and good slope (0.9); however, the intercept value (4.69) indicated that, at low concentrations, the "home-made" device gave lower values than those determined with the conventional monitor. Concentrations reported for the conventional device ranged from 11 to 189 ppm.

Benson and Boyce[51] field tested the Monsanto Poropak S device in Great Britain. Conventional samplers consisted of pumps and Poropak N polymer tubes. Sixty-five pairs of samples were obtained, and the range of acrylonitrile measured by the tubes was 0.13 to 21.65 ppm. Regression analysis of their data indicates only fair correlation (0.63), a low slope (0.46), and a negative intercept (−2.06). These values appear to result from the apparent inability of the passive device to accurately detect concentrations less than 0.5 ppm. Also, comparisons between values over the lower half of concentrations sampled showed considerable scatter.

The final field study to be discussed suggests perhaps the most serious discrepancies resulting from use of charcoal passive dosimeters.[61] This study was performed by NIOSH personnel in conjunction with industry-wide studies of the dry-cleaning, screen printing, and boat manufacturing industries, and also included one viscose rayon and one cellophane plant. Carbon disulfide, perchloroethylene, toluene, methylisobutyl ketone (MIBK), styrene, and acetone were sampled using the 3M OVM, the GASBADGE, and active systems with charcoal tubes. The presentation of the study design is not clear, but it appears that area samples involved all three devices while personal samples involved charcoal tubes and only one of either passive device. In that this study involves six compounds in 64 plants, the volume of data is quite large. In addition to regression analysis, paired t-tests and Wilcox signed rank tests were performed by the authors to determine equivalence of data sets. As noted earlier the use of t-tests for determination of equivalence has been questioned.[19]

Table IV shows the primary results of this study. As can be seen, the range of correlation coefficients (r) for most compounds was quite large. Although 12 plants were surveyed for toluene and MIBK, the data were grouped together, and therefore ranges of the correlation coefficients could not be determined. For carbon disulfide, one plant was surveyed with the OVM and GASBADGE, and one was surveyed with the GASBADGE only. For the ranges of r reported in Table IV, the upper values are quite acceptable, with the exception of carbon disulfide using the GASBADGE. However, the correlation coefficient for carbon disulfide using the OVM was 0.95. The correlation data can be summed up as being extremely variable. Table IV also reveals that concentration had an effect on the correlation coefficient for three of the compounds, though this was true for both monitors only when measuring acetone concentrations. Regression slopes were as variable as the correlation coefficients. The authors tested the slopes to see if they were significantly different from zero, and for acetone and carbon disulfide a difference could not be demonstrated for several of their data sets. This indicated that there was no relationship between the results obtained with the active system and those obtained with the passive dosimeter. For other compounds, it would have been useful to test the difference of the slope from one, which if not significantly different would indicate agreement of the two methods.

In tests of equivalence of data sets, the authors noted that for all plant data combined, only toluene showed equality, and this for the charcoal tube-GASBADGE (CT-GB) comparison. However, when results from individual plants are used, the comparison outcomes are quite variable. For perchloroethylene, equality was reported for one of three CT-BG comparisons and for one of two CT-3M sets. For styrene, two of six CT-GB and no CT-3M comparisons showed equality. For acetone, three of five CT-3M comparisons and one of six CT-GB data sets showed equality. In addition, GB-OVM comparisons showed equality in 6 of 17 comparisons. It is obvious that repeatability was not demonstrated in this study. Whether the problem involves the dosimeters, investigative or laboratory techniques, and or environmental conditions cannot be determined. In the only other field study of more than one plant, Hickey and Bishop[9] also reported some problems with the consistency of observations. These limited results clearly demonstrate the need for additional field studies of passive dosimeters as compared with standard monitoring techniques.

discussion

Passive dosimetry (monitoring) is a rapidly developing technology as witnessed by the proliferation of devices and applications since Palmes and Gunnison introduced their concepts just under ten years ago.[22] The latest entry into the field comes from the MSA Company and involves an adaptation of their length-of-stain direct reading tubes for inorganic gases[62] which incorporates the application of molecular diffusion and a chemically impregnated paper as the sampling medium. Although research results are not available, as a first approximation one might assume that these devices have precisions and biases similar to those of conventional detector tubes.

For any new technology to be accepted and used by practicing professionals, the development of a body of knowledge demonstrating efficacy is necessary. With environmental monitoring techniques, the determination of the efficacy usually starts in the laboratory and culminates in the field. In the case of passive monitors, a body of knowledge based on laboratory testing is rapidly being developed. Of the vari-

TABLE IV
Major Results of a Field Study for Organic Vapors[61]

Substance	Comparison	Overall r	Range of r	Concentration Dependency
Perchloro-ethylene	CT-GB	0 62	0 62-0 99	
	CT-3M	0 86	0 84-0 94	
Styrene	CT-GB	0 82	0 65-0 97	
	CT-3M	0 76	0 48-0 86	
Acetone	CT-GB	0 38	0 36-0 86	Yes
	CT-3M	0 45	0 25-0 83	Yes
Toluene	CT-GB	0 80	NA	
	CT-3M	0 91	NA	Yes
MIBK	CT-GB	0 88	NA	
	CT-3M	0 79	NA	
CS	CT-GB	0 30	0 03-0 38	
	CT-3M	0 95	NA	Yes

ables that have been studied, three appear to uniquely affect a diffusion monitors accuracy in measuring airborne concentrations of gases or vapors. The most important factor appears to be determination of the contaminants' diffusion coefficient (or the sampling rate when the dosimeter's geometry is also considered), the wind velocity at the dosimeter face, and the relative humidity of the sampled air. As discussed earlier, there are also a variety of potential sources of error, such as interfering contaminants, sorbent capacity and problems associated with analytical determinations, which are common to both passive and active measurement techniques.

Laboratory determination of sampling rates (DA L) for a specific monitor and a specific contaminant are important and are being provided by several dosimeter manufacturers for an ever increasing number of compounds. Once an appropriate sampling rate has been determined, corrections for field use, specifically for temperature variations, can be made. The main problem would involve situations where the environmental temperature fluctuated widely (more than 25 °C) and went unnoticed, a very unlikely condition.

The research on effects of face velocities demonstrate that few problems should be encountered where dosimeters are worn by workers as personal monitoring devices.[1,12,24,25,32] Their use as area monitors should be carefully evaluated to ensure that stagnant atmospheres (velocities less than 7.5 cm sec) are not involved. High wind velocities (at least what would normally be encountered in the workplace) or wind direction do not appear to have adverse effects on dosimeters with wind screens.

Of greatest concern as a result of reviewing the literature on laboratory testing of passive dosimeters is not the results but rather the thoroughness of their presentation. As demonstrated in Tables I and II, where statistical analyses are presented by researchers, or where sufficient data are presented to allow the reader to determine bias and precision, the results are very encouraging. Unfortunately the presentation of experimental design, as well as sufficient data and or statistical analyses, are often lacking. This is true for some individual researchers as well as for several manufacturers of the devices, especially those for inorganic compounds. If one recommendation regarding laboratory testing is made, would be that those researchers involved in the evaluation of passive dosimeters in the laboratory take the time to report the conditions of their experiments, especially equipment used and procedures for determining "known" concentrations, and as much detail about their results as possible. If summarized data are presented, the author should present the known concentration at each level, where levels are determined by concentration and time, the number of observations made with passive dosimeters, and the average value and standard deviation of the results. Statistical analyses again at each level tested, should involve determination of the coefficient of variation (precision) and the bias as described in equations (7) and (8), respectively. Once the evaluations are made at the various test levels, the determination of a pooled precision and bias is appropriate. In addition to these measurements, researchers may also choose to present an overall system accuracy. To develop a better understanding of appropriate statistical techniques and their application to passive dosimetry, a review of Lautenberger *et al.* is recommended.[11]

For most active monitoring systems used in industrial hygiene the random sampling error is usually associated with the pump and is traditionally set at ± 5 percent.[16] In many cases, especially for the measurement of organic vapors, the analytical procedures and consequently their associated errors are equivalent for both passive and active systems. Nevertheless, both systems have random error; consequently, one should not expect perfect agreement of the results of comparisons obtained under field test conditions. Another factor complicating the evaluation of field results is the greatly increased possibility for the introduction of operator, or systematic, errors. Since active systems require mechanical pumps, the potential for operator error would seem to be greater than for passive systems.

Overall, it is apparent that existing field observations comparing passive dosimeters with standard monitoring methods are highly varied. While some studies demonstrate good correlation and slope,[9,25,45] others show only good correlation,[42] or are extremely varied for both categories.[61] Collectively, these references neither support nor refute the use of passive dosimeters. Certainly environmental factors affect active systems as well as passive systems. In theory a case can be made that environmental factors (wind and humidity) affect passive systems to the greatest extent, while temperature and pressure variations most greatly affect active systems. On the other hand one can also state that poor experimental quality control may affect such factors as contamination, time measurement error, and analytical error. Of course, chemical interferences may affect both systems.

As with laboratory experimentation, recommendations regarding the field testing of passive dosimeters involve a plea for better reporting of both field conditions and results of analysis. First, for both personal and area monitoring, the estimation and or measurement of face velocity is impor-

tant. Of equal importance is the reporting of airborne contaminants other than the one(s) of interest and environmental variables including temperature, pressure, and relative humidity along with information as to their variation over the period of observation. Again, if raw data cannot be presented, the reported results for each level tested (X value as determined by the standard method) should include the number of observations made with passive dosimeters, and their associated mean and coefficient of variation. Statistical evaluations also should include a regression analysis of the data as outlined earlier. Undoubtedly, additional research is needed on the effect of not considering the error associated with the supposedly independent (X) variable.

In summary, passive dosimeters show great promise as an important tool. The results presented in Tables I and II indicate that the precisions of the dosimeters are essentially equivalent to conventional techniques and in many cases the additional five percent error associated with mechanical pumps makes passive dosimeter systems even more attractive. This, coupled with their ease of use, lack of required maintenance, acceptance by workers due to light weight, and unnecessary calibration make passive dosimeters extremely advantageous. Certainly they will not replace conventional methods, as these have their place, especially for area sampling. The continued and growing use of passive dosimeters, however, should generate additional data documenting their reliability and eliminating doubts about their usefulness.

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A simple method for the determination of desorption fficiencies of organic compounds collected on the 3M 3500 Organic Vapor Monitor has been developed. The technique involves the introduction of the organic compound, in the liquid stat , onto a piece of filter paper placed between the elutriation cap and the diffusion plate of the organic vapor monitor. This is accomplished by direct injection of the organic compound through the center elutriation port of the monitor cap. The port is closed and the organic compound is given sufficient time to vaporize and consequently be adsorbed by the charcoal sorbent. The filter paper is removed and analyzed as a separate sample to assure complete transfer of the organic compound. All samples are desorbed by a suitable solvent and analyzed by gas chromatography. Desorption efficiencies for methyl chloroform, benzene, heptane, acetone, dioxane, isobutanol and ethyl acetate are determined. A comparison with results by the phase equilibrium method is made.

Determination of desorption efficiencies in the 3M 3500 Organic Vapor Monitor

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introduction

For a quantitative determination of the amount of contaminant collected on any sorbent. it is necessary to know how much of the adsorbate is eluted out. The ratio of the measured weight recovered by the desorbing solvent to the known weight of contaminant added to the adsorbent is defined as the desorption efficiency or recovery coefficient.

One procedure for determining recovery coefficients from charcoal tubes involves direct injection of a known amount of the liquid compound into the activated charcoal using a microliter syringe.[1] After overnight standing, the sample is eluted with an appropriate solvent and analyzed by gas chromatography Especially for polar compounds, the results from this method are often inconsistent.[2] In addition, direct spiking of liquid does not correspond to actual field sampling of vapor from the atmosphere. Liquid spiking may be a source of error, since the compound is localized in a small area of the sorbent rather than being uniformly distributed throughout the sorbent.

In activated charcoal sorbent, the spaces, called pores, between the individual microcrystallites may be further classified as:

a) micropores, with effective radii of less than 18-20 Angstroms, comprising a minimum of 95% of the total surface area;

b) mesopores, also called transitional pores, where capillary condensation takes place: with effective radii of roughly 20-1000 Angstroms which make up not more than 5% of the total surface area; and

c) macropores with effective radii of more than 1000 Angstroms which are too big to be filled by capillary condensation.[3]

The ratio in which the different classes of pores are present in a specific type of activated charcoal dictates its suitability for specific purposes. Microporous activated carbons are most effective for adsorption of small concentrations of gases and vapors. On the other hand, mesoporous carbons are better used to recover industrial solvent vapors. The pore size distribution determines the adsorption, desorption processes involved and also the resulting efficiencies. Micropores may be suitable for efficient adsorption of vapors but consequent desorption from them is difficult since there may be no room for a displacing agent to enter.[4]

Consider a model picture of the microcrystallites of activated charcoal.[5] During a vapor spike, schematically shown in Figure 1a, we can imagine the molecules first entering the macropores, then the mesopores and finally the micropores where some interactions with the walls tend to increase retention and decrease recovery by a solvent. However, a liquid spike would be concentrated in spots and tend to wet the walls of the mesopores. Imagine now that we have menisci as in Figure 1b which exhibit some surface tension. It has been verified experimentally that the vapor pressure of solvents in capillaries of a few microns radius are lowered 10-80 times more than what the Kelvin Equation predicts.[6] The Kelvin Equation relates the normal vapor pressure of a liquid (assuming a flat surface) to that observed over the curved surface of the liquid given its spherical surface radius. A decrease in vapor pressure makes it harder for the liquid to vaporize and occupy the micropores. The liquid would tend to stay in the mesopores where wall effects are small and the energy of adsorption is less. Consequent elution would then result in higher recoveries.

With these possible deficiencies of liquid spiking in mind, the vapor-state spiking technique for the 3M 3500 Organic Vapor Monitor was developed.

Figure 1a — Concept of molecules in activated charcoal pores

Figure 1b — Meniscus formation by molecules in activated charcoal pores

experimental

gas chromatography

A Hewlett-Packard 5840A gas chromatograph equipped with a flame ionization detector and an automatic sampler, Model 7672A, was used. The columns were 15% Carbowax 20M on 80/100 mesh Supelcoport, 2 m × 6.4 mm o.d. glass (6 ft × 1/4 in.); 15% Carbowax 20M on 80/100 mesh Chromosorb W, 2.3 m × 3.2 mm o.d. stainless steel (7 1/2 ft × 1/8 in.); 10% SP-2100 on 80/100 mesh Supelcoport, 3.0 m × 3.2 mm o.d. stainless steel (10 ft × 1/8 in.); 0.1% SP-1000 on 80/100 mesh Carbopack C, 1.8 m × 3.2 mm o.d. stainless steel (6 ft × 1/8 in.); and Chromosorb 101, 100/120 mesh, 0.9 m × 6.4 mm o.d. glass (3 ft × 1/4 in.).

Samples to be analyzed were contained in 1 ml glass vials sealed with Teflon-lined septum caps.

procedure

For the vapor-state spiking technique, Whatman #4 filter paper, 1.6 cm in diameter, was placed between the elutriation cap and the diffusion plate in each 3M 3500 Organic Vapor Monitor. The elutriation caps were snapped on and a known quantity of the organic solvent under study was injected onto the paper through the center elutriation port. The port was closed and the system was allowed to stand at room temperature for 16-24 hours before elution to give sufficient time for total transfer of the organic compound from the filter paper to the sorbent.

Gaseous compounds, *i.e.*, ethyl chloride, were studied by inserting a rubber septum into the center elutriation port and injecting the known quantity of gas through the septum with a gastight syringe. In this case, the filter paper was not impregnated. The system was allowed to stand at room temperature overnight prior to elution.

Another alternative for gas spikes was to cover the 3M 3500 Organic Vapor Monitor with a cylindrical glass dome equipped with an injection port and a Teflon-lined septum, as in Figure 2. To insure against leakage, Parafilm® was wrapped around the glass at contact points with the monitor. The known amount of gas was then injected through the septum into the air above the monitor. After standing 16-24 hours, the dome, barrier film and the barrier film holder of the monitor were removed. The elutriation cap was then snapped into place and both ports closed.

A measured volume (1.5 ml) of eluting solvent was injected into each monitor through the center port using an automatic dispenser. The port was resealed and the sample was allowed to elutriate for one-half hour with occasional gentle agitation. After decanting the eluate from the monitor into glass vials, analysis by gas chromatography was performed on each sample. The filter paper of each sample was separately analysed.

Standards were prepared by spiking an equivalent amount of the organic compound into sealed glass vials containing 1.5 ml of the appropriate eluent using the same injection

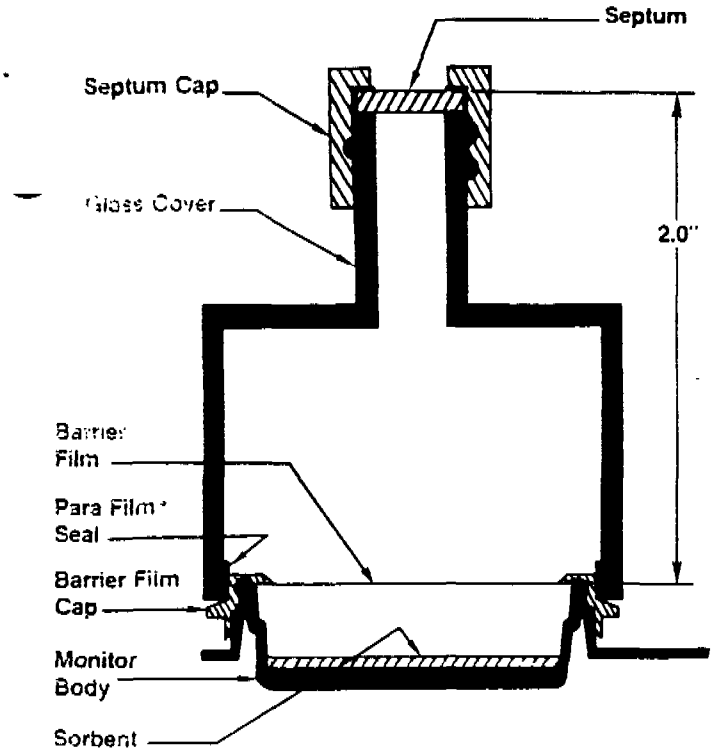

Figure 2 — Cylindrical glass dome for gas spiking.

syringe. The punctured seals were replaced by new ones and the standards prepared were kept in the refrigerator at 5 °C. Before analysis, they were allowed to come to room temperature.

A parallel experiment using the Phase Equilibrium method was run simultaneously.[7] Working solutions of organic compounds diluted with the appropriate solvent were prepared. The charcoal sorbent in some monitors was removed and 1.5 mL of the working solution were added through the center port of the elutriation cap. These were used as the standards. An equal aliquot was added to another set of monitors which still contained the charcoal sorbent.

Both sets of monitors for each organic compound under investigation were allowed to elutriate for one-half hour at room temperature, decanted into glass vials, sealed, and analyzed by gas chromatography.

results and discussion

The sampling rates of the 3M 3500 Organic Vapor Monitor for acetone, benzene, dioxane, ethyl acetate, ethyl chloride, heptane, isobutanol, methyl chloroform and methyl ethyl ketone are listed in Table I. The Threshold Limit Value - Time-Weighted-Average (TLV-TWA) concentration for each compound was taken from the ACGIH handbook.[8] The amount spiked was the number of milligrams expected in a monitor which samples a concentration of one-half TLV-TWA for four hours except when it was beyond the capacity of the monitor. For those cases, 75% of the capacity was used.

Considering benzene with a sampling rate of 35.5 cc/min and a TLV-TWA of 30 mg/m^3, we expect 0.1 mg adsorbed by the monitor at one-half TLV-TWA for four hours (mg = 35.5 cc/min × 60 min/hr × 4 hrs × 30 mg/m^3 × 1/2 × 1 m^3/10^6 cc).

A comparison of desorption efficiencies obtained by the vapor-state spike and by the Phase Equilibrium method is shown in Table II. The results of five determinations per experiment are given with standard deviations. There is close agreement between the two methods except for the results of isobutanol and ethyl chloride. Both of these were eluted with methylene chloride while the rest were desorbed with carbon disulfide.

Table III lists some physical constants for methylene chloride, isobutanol and ethyl chloride. When two atoms with different electronegativities are bonded together, the bonding electrons spend a greater time near the atom of higher electronegativity, so that there is a net positive charge at the other atom and the molecule takes on a polar character. The dielectric constant and dipole moment are measures of polarity; the higher the value, the more polar is the compound. The measured diffusion coefficients for methylene chloride and isobutanol are listed while that for ethyl chloride is a theoretical value from the Hirschfelder Equation.[9]

TABLE I
Compound Guide for Determination of Desorption Efficiencies in the 3M 3500 Organic Vapor Monitor

Compound	OVM Sampling Rate cc/min	TLV-TWA[8] PPM	TLV-TWA[8] mg/m^3	Spiked Amount* mg
Acetone	40.1	(1000)	(2400)	2.2
Benzene	35.5	10	30	0.1
Dioxane	34.5	(50)	(180)	0.8
Ethyl Acetate	34.5	400	1400	5.8
Ethyl Chloride	38.8	1000	2600	0.2
Heptane	28.9	400	1600	5.6
Isobutanol	35.9	50	150	0.6
Methyl Chloroform	30.9	350	1900	7.0
Methyl Ethyl Ketone	36.3	200	590	2.6

*Amount sampled by the monitor at a concentration of 1/2 TLV-TWA for four hours except when it is beyond the capacity of the monitor. For those cases, the amount spiked is 75% of the capacity.

The molecular radius of the compounds were predicted from atomic volumes.[10] From our concept of the activated charcoal surface with the different pore structures, we can imagine that with the presence of both methylene chloride and isobutanol in the Phase Equilibrium method, there results a competition between the two compounds as they travel into the pores. The greater mobility of the smaller molecule, in this case, methylene chloride, also results in faster diffusion into the micropores.

Another contributing factor is the higher concentration of methylene chloride, present as the solvent, which allows for more collision and interaction with the surface than the isobutanol, permitting deep penetration into the finer pores. There exists, therefore, a higher concentration of isobutanol in the mesopores which have lower energies of adsorption. Upon decantation and analysis of the resulting solution, high isobutanol recoveries are obtained.

Using vapor-state spiking, there is no competitor with isobutanol for the active sites on the charcoal surface, so the molecules are free to seek even the fine pores which have higher energies of adsorption.

We have observed that a 30 minute interval was sufficient to transfer all the spiked isobutanol from the filter paper to the charcoal. For an experiment, several monitors were spiked with isobutanol and allowed to stand for 0.5, 1.0, 4.0 and 24 hours prior to elution and analysis. Even at 30 minutes, no trace of isobutanol was found on the filter paper. Table IV shows that a longer adsorption time can cause lower recoveries for isobutanol.

More molecules are adsorbed in the micropores, thus, desorption is difficult. Since analysis of samples does not immediately follow the field sampling, it is therefore recommended that the method used for determination of desorption efficiencies be designed to duplicate actual use situations as closely as possible.

The effect of time was also studied for the Phase Equilibrium method using ethyl chloride. Aliquots of a prepared solution of ethyl chloride in methylene chloride were added to several organic vapor monitors and were analyzed at different time intervals, the results in Table V show a change in the adsorption desorption process within 24 hours, giving an average desorption efficiency of 1.02 ± 0.01.

TABLE II
Comparison of Desorption Efficiencies

Compound	Desorption Efficiencies	
	Vapor Spike	Phase Equilibrium
Acetone	0.93 ± 0.03	0.94 ± 0.01
Benzene	0.99 ± 0.01	0.99 ± 0.01
Dioxane	0.92 ± 0.03	0.88 ± 0.02
Ethyl Acetate	0.98 ± 0.03	0.98 ± 0.01
Ethyl Chloride	0.81 ± 0.03	1.01 ± 0.01
Heptane	1.04 ± 0.03	1.03 ± 0.01
Isobutanol	0.90 ± 0.02	1.04 ± 0.01
Methyl Chloroform	1.02 ± 0.02	1.02 ± 0.01

These data also demonstrated that the 3M 3500 Organic Vapor Monitor does not leak and that the monitor materials are inert both chemically and physically. The efficient seal of the organic vapor monitor was further verified by a test wherein monitors with the elutriation caps on were exposed to a chamber saturated with xylene vapors for two hours. A control sample without a cap was used and this collected about 59 mg of xylene while the capped ones only showed trace amounts.

The results from an investigation of concentration effects on desorption efficiencies by both vapor-state spiking and Phase Equilibrium methods are summarized in Table VI. The concentrations chosen were all less than the suggested spiked amount of 2.6 mg MEK 1.5 mL carbon disulfide (see Table I).

The unpaired t statistical evaluation of the data showed no significant differences between the desorption efficiencies of concentration Levels II and III for both methods.[11] At a confidence level of 95%, the test statistic t values for the vapor-state spiking method and for the Phase Equilibrium method were 0.24 and −0.89, respectively. Desorption efficiency values at concentration Level I were significantly different from the pooled results of concentration Levels II and III for both methods. At low concentrations, the walls of the pores in the sorbent strongly hold onto the molecules of the compound and the eluent cannot completely sever all bonds formed, thus creating a case of irreversible adsorption.

A comparison between a vapor-state spike and a directly injected liquid spike onto the charcoal sorbent of the 3M

TABLE III
Physical Constants[12,13]

	Methylene Chloride	Isobutanol	Ethyl Chloride
Molecular Formula	CH_2Cl_2	$C_4H_{10}O$	C_2H_5Cl
Molecular Weight	84.94	74.12	64.52
Boiling Point	39.75 °C	108 °C	12.3 °C
Dielectric Constant	1.0065 (gas) 9.08 (liq.)	15.8 (liq.)	1.0132 (gas)
Dipole Moment	1.60 debyes	1.64 debyes	2.05 debyes
Diffusion Coefficient	0.1037 $cm^2/sec.$	0.0880 $cm^2/sec.$	0.1134 $cm^2/sec.$
Molecular Radius	4.754 Å	5.637 Å	4.856 Å

TABLE IV
Effect of Time on Vapor State Spiking of Isobutanol

Adsorption Time (hrs)	Desorption Efficiency
0.5	0 97
1.0	0.99
4 0	0.98
24.0	0.91

TABLE V
Effect of Time on Phase Equilibrium Method for Ethyl Chloride

Adsorption Time (hrs)	Desorption Efficiency
0.5	1.02
1.0	1 01
2 0	1.01
3.0	1.03
5.0	1.01
6 0	1 02
7 0	1 02
24 0	1 01
Average	1 02 ± 0 01

3500 Organic Vapor Monitor was made and the results are listed in Table VII. No difference in the desorption efficiencies of MEK by both methods was seen when overnight adsorption was utilized (test statistic t was -0.973 at $\alpha = 0.05$). The effect of different adsorption time intervals was studied. Results are given in Table VIII. It was noted that complete transfer of the compound from the filter paper to the sorbent was accomplished within 30 minutes prior to elution.

No significant change was observed even after 24 hours adsorption time by the vapor-state spike method. On the other hand, a slight decrease in desorption efficiency was observed using the direct liquid spike method.

summary

The efficiency of elution recovery processes can be affected by many variables, including sample introduction, adsorption desorption time, chemical structures and concentration. Much of the variability can be explained by differences in the mechanisms of filling and emptying the pores of specific shape and size. Since the filling of pores of the sorbent in the 3M 3500 Organic Vapor Monitor in an actual field sampling of vapors from the atmosphere runs parallel to that in the vapor-state spiking method, more reliable desorption efficiencies by this latter method is expected.

Although it was shown that no differences were found between the vapor-state spiking method and the direct liquid spiking method for the determination of the MEK desorption efficiency, other factors like concentrations, the length of time of adsorption and chemical structure may make

TABLE VI
Effect of Concentration on Desorption Efficiency of MEK

Concentration (μg/mL)	Vapor-State Spiking Technique	Phase Equilibrium Technique
Level I		
80.54	0.70	0.94
	0.69	0.87
	0.69	0.92
	0.68	0.86
	0 70	0.85
Average.	0.69 ± 0 01	0.89 ± 0.04
Level II		
805.4	0.90	0.91
	0.89	0.95
	0.90	0.93
Average.	0.90 ± 0.01	0.93 ± 0 02
Level III		
1610.8	0.87	1.02
	0.90	0.93
	0.92	0 95
	0.89	0.93
	0 89	0 93
Average:	0.89 ± 0.02	0.95 ± 0 04

G.C. Column: 15% Carbowax 20M on 80/100 mesh Supelcoport, 1.8 m × 6.4 mm o.d. glass (6 ft. × 1/4 in.)
Temperature. Isothermal 60 °C
Carrier Gas: Helium 30.3 mL/min.
MEK Retention Time. 1 25 minutes

TABLE VII
Comparison of Desorption Efficiencies of MEK

Vapor Spike		Liquid Spike	
0.92		0.91	
0.92		0.92	
0.89		0.92	
0.91		0.92	
0.92		0.92	
Average.	0.91 ± 0.01	Average:	0.92 ± 0.004

TABLE VIII
Effect of Time on Desorption Efficiency of MEK

Adsorption Time (hrs)	Desorption Efficiency: Vapor State Spike Method	Desorption Efficiency: Liquid Spike Method
0.5	0.91	0.94
1.0	0.90	0.92
4.0	0.92	0.91
24.0	0.90	0.91

greater differences. In our experiment, we used the suggested spiked amount for MEK representing an exposure of one-half TLV-TWA for four hours. Measuring lower concentrations in the field may produce 5-29% differences depending on whether the determination of the desorption efficiency of MEK is doen by the vapor-state spike or the Phase Equilibrium techniques. The differences seem to be more pronounced with polar compounds. The results of the two techniques agreed when less polar to nonpolar compounds were studied.

The time of adsorption to achieve equilibrium of the adsorbed molecules with the structural atoms of the surface of the sorbent affects the vapor-state spiking method more than the Phase Equilibrium technique.

The vapor-state spiking technique used to determine 3M published values is therefore recommended for the determination of desorption efficiencies using the 3M 3500 Organic Vapor Monitor.

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Determination of Desorption Efficiencies in the 3M 3500 Organic Vapor Monitor

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A simple method for the determination of desorption efficiencies of organic compounds collected on the 3M 3500 Organic Vapor Monitor has been developed. The technique involves the introduction of the organic compound, in the liquid state, onto a piece of filter paper placed between the elutriation cap and the diffusion plate of the organic vapor monitor. This is accomplished by direct injection of the organic compound through the center elutriation port of the monitor cap. The port is closed and the organic compound is given sufficient time to vaporize and consequently be adsorbed by the charcoal sorbent. The filter paper is removed and analyzed as a separate sample to assure complete transfer of the organic compound. All samples are desorbed by a suitable solvent and analyzed by gas chromatography. Desorption efficiencies for methyl chloroform, benzene, heptane, acetone, dioxane, isobutanol and ethyl acetate are determined. A comparison with results by the phase equilibrium method is made.

I. INTRODUCTION

For a quantitative determination of the amount of contaminant collected on any sorbent, it is necessary to know how much of the adsorbate is eluted out. The ratio of the measured weight recovered by the desorbing solvent to the known weight of contaminant added to the adsorbent is defined as the desorption efficiency or recovery coefficient.

One procedure for determining recovery coefficients from charcoal tubes involves direct injection of a known amount of the liquid compound into the activated charcoal using a microliter syringe.[1] After overnight standing, the sample is eluted with an appropriate solvent and analyzed by gas chromatography. Especially for polar compounds, the results from this method are often inconsistent.[2] In addition, direct spiking of liquid does not correspond to actual field sampling of vapor from the atmosphere.

Liquid spiking may be a source of error, since the compound is localized in a small area of the sorbent rather than being uniformly distributed throughout the sorbent.

In activated charcoal sorbent, the spaces, called pores, between the individual microcrystallites may be further classified as:

2) micropores, with effective radii of less than 18-20 Angstroms, comprising a minimum of 95% of the total surface area;

b) mesopores, also called transitional pores, where capillary condensation takes place; with effective radii of roughly 20-1000 Angstroms which make up not more than 5% of the total surface area; and

c) macropores with effective radii of more than 1000 Angstroms which are too big to be filled by capillary condensation.[3]

The ratio in which the different classes of pores are present in a specific type of activated charcoal dictates its suitability for specific purposes. Microporous activated carbons are most effective for adsorption of small concentrations of gases and vapors. On the other hand, mesoporous carbons are better used to recover industrial solvent vapors. The pore size distribution determines the adsorption/desorption processes involved and also the resulting efficiencies. Micropores may be suitable for efficient adsorption of vapors but consequent desorption from them is difficult since there may be no room for a displacing agent to enter.[4]

Let us consider a model picture of the microcrystallites of activated charcoal.[5] During a vapor spike, schematically shown in Figure 1a, we can imagine the molecules first entering the macropores, then the mesopores and finally the micropores where some interactions with the walls tend to increase retention and decrease recovery by a solvent. However, a liquid spike would be

concentrated in spots and tend to wet the walls of the mesopores. Imagine now that we have menisci as in Figure 1b which exhibit some surface tension. It has been verified experimentally that the vapor pressure of solvents in capillaries of a few microns radius are lowered 10-80 times more than what the Kelvin Equation predicts.[6] The Kelvin Equation relates the normal vapor pressure of a liquid (assuming a flat surface) to that observed over the curv d surface of the liquid given its spherical surface radius. A decrease in vapor pressure makes it harder for the liquid to vaporize and occupy the micropores. The liquid would tend to stay in the mesopores where wall effects are small and the energy of adsorption is less. Consequent elution would then result in higher recoveries.

With these possible deficiencies of liquid spiking in mind, the vapor-state spiking technique for the 3M 3500 Organic Vapor Monitor was developed.

II. EXPERIMENTAL

A. Gas Chromatography

A Hewlett-Packard 5840A gas chromatograph equipped with a flame ionization detector and an automatic sampler, Model 7672A, was used. The columns were 15% Carbowax 20M on 80/100 mesh Supelcoport (6 ft. x 1/4 in. o.d. glass), 15% Carbowax 20M on 80/100 mesh Chromosorb W (7-1/2 ft. x 1/8 in. o.d. stainless steel), 10% SP-2100 on 80/100 mesh Supelcoport (10 ft. x 1/8 in. o.d. stainless steel), 0.1% SP-1000 on 80/100 mesh Carbopack C (6 ft. x 1/8 in. o.d. stainl ss steel) and Chromosorb 101, 100/120 mesh (3 ft. x 1/4 in. o.d. glass).

Samples to be analyzed were contained in 1 ml glass vials sealed with Teflon-lined septum caps.

B. Procedure

For the vapor-state spiking technique, Whatman #4 filter paper, 1.6 cm in diameter, was placed between the elutriation cap and the diffusion plate in each 3M 3500 Organic Vapor Monitor. The elutriation caps were snapped on and a known quantity of the organic solvent under study was injected onto the paper through the center elutriation port. The port was closed and the system was allowed to stand at room temperature for 16-24 hours before elution to give sufficient time for total transfer of the organic compound from the filter paper to the sorbent.

Gaseous compounds, i.e., ethyl chloride, were studied by inserting a rubber septum into the center elutriation port and injecting the known quantity of gas through the septum with a gas-tight syringe. In this case, the filter paper was eliminated. The system was allowed to stand at room temperature overnight prior to elution.

Another alternative for gas spikes was to cover the 3M 3500 Organic Vapor Monitor with a cylindrical glass dome equipped with an injection port and a Teflon-lined septum, as in Figure 2. To insure against leakage, Parafilm® was wrapped around the glass at contact points with the monitor. The known amount of gas was then injected through the septum into the air above the monitor. After standing 16-24 hours, the dome, barrier film and the barrier film holder of the monitor were removed. The elutriation cap was

then snapped into place and both ports closed.

A measured volume (1.5 ml) of eluent was added to each monitor through the center port using an automatic dispenser. The port was resealed and the sample was allowed to elutriate for 1/2 hour with occasional gentle agitation. After decanting the eluate from the monitor into glass vials, analysis by gas chromatography was performed on each sample. The filter paper of each sample was separately analyzed.

Standards were prepared by spiking an equivalent amount of the organic compound into sealed glass vials containing 1.5 ml of the appropriate eluent using the same injection syringe. The punctured seals were replaced by new ones and the standards prepared were kept in the refrigerator at 5°C. Before analysis, they were allowed to come to room temperature.

A parallel experiment using the Phase Equilibrium method was run simultaneously.[7] Working solutions of organic compounds diluted with the appropriate solvent were prepared. The charcoal sorbent in some monitors was removed and 1.5 ml of the working solution were added through the center port of the elutriation cap. These were used as the standards. An equal aliquot was added to another set of monitors which still contained the charcoal sorbent. Both sets of monitors for each organic compound under investigation were allowed to elutriate for 1/2 hour at room temperature, decanted into glass vials, sealed, and analyzed by gas chromatography.

III. RESULTS AND DISCUSSION

The sampling rates of the 3M 3500 Organic Vapor Monitor for acetone, benzene, dioxane, ethyl acetate, ethyl chloride, heptane, isobutanol, methyl chloroform and methyl ethyl ketone are listed in Table I. The Time-Weighted-Average concentration for each compound was taken from the ACGIH handbook.[8] The amount spiked was the number of milligrams expected in a monitor which samples a concentration of 1/2 TWA for 4 hours except when it was beyond the capacity of the monitor. For those cases, 75% of the capacity was used.

Considering benzene with a sampling rate of 33.0 cc/min and a TWA of 30 mg/m^3, we expect 0.1 mg adsorbed by the monitor at 1/2 TWA for 4 hours (mg = 33.0 cc/min x 60 min/hr x 4 hrs x 30 mg/m^3 x 1/2 x $1m^3/10^6$ cc).

A comparison of desorption efficiencies obtained by the vapor-state spike and by the Phase Equilibrium method is shown in Table II. The results of five determinations per experiment are given with standard deviations. There is close agreement between the two methods except for the results of isobutanol and ethyl chloride. Both of these were eluted with methylene chloride while the rest were desorbed with carbon disulfide.

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Another contributing factor is the higher concentration of methylene chloride, present as the solvent, which allows for more collision and interaction with the surface than the isobutanol, permitting deep penetration into the finer pores.

There exists, therefore, a higher concentration of isobutanol in the mesopores which have lower energies of adsorption. Upon decantation and analysis of the resulting solution, higher isobutanol recoveries are obtained.

Using vapor-state spiking, there is no competitor with isobutanol for the active sites on the charcoal surface, so the molecules are free to seek even the fine pores which have higher en rgies of adsorption.

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The effect of time was also studied for the Phase Equilibria method using ethyl chloride. Aliquots of a prepared solution of ethyl chloride in methylene chloride were added to several organic vapor monitors and were analyzed at different time intervals. The results in Table V show no change in the adsorption/desorption process within 24 hours, giving an average desorption efficiency of 1.02 ± 0.01.

These data also demonstrated that the 3M 3500 Organic Vapor Monitor does not leak and that the monitor materials are inert both chemically and physically. The efficient seal of the organic vapor monitor was further verified by a test wherein monitors

with the elutriation caps on were exposed to a chamber saturated with xylene vapors for 2 hours. A control sample without a cap was used and this collected about 59 mg of xylene while the capped ones only showed trace amounts.

The results from an investigation of concentration effects on desorption efficiencies by both vapor-state spiking and Phase Equilibria methods are summarized in Table VI. The concentrations chosen were all less than the suggested spiked amount of 2.2 mg MEK/1.5 ml carbon disulfide (see Table I).

The unpaired t statistical evaluation of the data[12] showed no significant differences between the desorption efficiencies of concentration Levels II and III for both methods. At a confidence level of 95%, the test statistic t values for the vapor-state spiking method and for the Phase Equilibrium method were 0.24 and -0.89, respectively. Desorption efficiency values at concentration Level I were significantly different from the pooled results of concentration Levels II and III for both methods. At low concentrations, the walls of the pores in the sorbent strongly hold onto the molecules of the compound and the eluent cannot completely sever all bonds formed, thus creating a case of irreversible adsorption.

A comparison between a vapor-state spike and a directly injected liquid spike onto the charcoal sorbent of the 3M 3500 Organic Vapor Monitor was made and the results are listed in Table VII. No difference in the desorption efficiencies of MEK by both methods was seen when overnight adsorption was utilized (test statistic t was -0.973 at $\alpha = 0.05$). The effect of

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IV. SUMMARY

The efficiency of elution recovery processes can be affected by many variables, including sample introduciton, adsorption/desorption time, chemical structures and concentration. Much of the variability can be explained by differences in the mechanisms of filling and emptying the pores of specific shape and size. Since the filling of pores of the sorbent in the 3M 3500 Organic Vapor Monitor in an actual field sampling of vapors from the atmosphere runs parallel to that in the vapor-state spiking method, we expect more reliable desorption efficiencies by this latter method.

Although it was shown that no differences were found between the vapor-state spiking method and the direct liquid spiking method for the determination of the MEK desorption efficiency, other factors like concentration, the length of time of adsorption and chemical structure may make greater differences. In our experiment, we used the suggested spiked amount for MEK representing an exposure of 1/2 TWA for 4 hours. Measuring lower concentrations in the field may produce 5-29% differences depending on whether the determination of the desorption efficiency of MEK is done by

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The time of adsorption to achieve equilibrium of the adsorbed molecules with the structural atoms of the surface of the sorbent affects the vapor-state spiking method more than the Phase Equilibrium technique.

We use the vapor-state spiking technique to determine our published values and recommend it for the determination of desorption efficiencies using the 3M 3500 Organic Vapor Monitor.

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TABLE I

COMPOUND GUIDE FOR DETERMINATION OF DESORPTION EFFICIENCIES IN THE 3M 3500 ORGANIC VAPOR MONITOR

Compound	OVM Sampling Rate cc/Min.	TWA[8] PPM	TWA[8] mg/m^3	Spiked Amount* mg
Acetone	35.4	(1000)	(2400)	6.9
Benzene	33.0	10	30	0.1
Dioxane	33.6	(50)	(180)	0.7
Ethyl Acetate	29.4	400	1400	4.9
Ethyl Chloride	40.1	1000	2600	0.2
Heptane	27.7	400	1600	5.3
Isobutanol	31.2	50	150	0.6
Methyl Chloroform	28.0	350	1900	6.4
Methyl Ethyl Ketone	31.2	200	590	2.2

*Amount sampled by the monitor at a concentration of 1/2TWA for four hours except when it is beyond the capacity of the monitor. For those cases, the amount spiked is 75% of the capacity.

TABLE II

COMPARISON OF DESORPTION EFFICIENCIES

Compound	Desorption Efficiencies	
	Vapor Spike	Phase Equilibrium
Acetone	0.93 ± 0.03	0.94 ± 0.01
Benzene	0.99 ± 0.01	0.99 ± 0.01
Dioxane	0.92 ± 0.03	0.88 ± 0.02
Ethyl Acetate	0.98 ± 0.03	0.98 ± 0.01
Ethyl Chloride	0.81 ± 0.03	1.01 ± 0.01
Heptane	1.04 ± 0.03	1.03 ± 0.01
Isobutanol	0.90 ± 0.02	1.04 ± 0.01
Methyl Chloroform	1.02 ± 0.02	1.02 ± 0.01

TABLE III

PHYSICAL CONSTANTS[13,14]

Molecular Formula	Methylene Chloride CH_2Cl_2	Isobutanol $C_4H_{10}O$	Ethyl Chloride C_2H_5Cl
Molecular Weight	84.94	74.12	64.52
Boiling Point	39.75°C	108°C	12.3°C
Dielectric Constant	1.0065 (gas) 9.08 (liq.)	- 15.8 (liq.)	1.0132 (gas) -
Dipole Moment	1.60 debyes	1.64 debyes	2.05 debyes
Diffusion Coefficient	0.1037cm^2/sec.	0.0880cm^2/sec.	0.1134cm^2/sec.
Molecular Radius	4.754 Å	5.637 Å	4.856 Å

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TABLE IV

EFFECT OF TIME ON VAPOR STATE SPIKING OF ISOBUTANOL

Adsorption Time (hrs)	Desorption Efficiency
0.5	0.97
1.0	0.99
4.0	0.98
24.0	0.91

TABLE V

EFFECT OF TIME ON PHASE EQUILIBRIUM METHOD FOR ETHYL CHLORIDE

Adsorption Time (hrs)	Desorption Efficiency
0.5	1.02
1.0	1.01
2.0	1.01
3.0	1.03
5.0	1.01
6.0	1.02
7.0	1.02
24.0	1.01
Average	1.02 ± 0.01

TABLE VI

EFFECT OF CONCENTRATION ON DESORPTION EFFICIENCY OF MEK

Concentration (μg/ml)		Vapor-State Spiking Technique	Phase Equilibrium Technique
Level I			
80.54		0.70	0.94
		0.69	0.87
		0.69	0.92
		0.68	0.86
		0.70	0.85
	Average:	0.69 ± 0.01	0.89 ± 0.04
Level II			
805.4		0.90	0.91
		0.89	0.95
		0.90	0.93
	Average:	0.90 ± 0.01	0.93 ± 0.02
Level III			
1610.8		0.87	1.02
		0.90	0.93
		0.92	0.95
		0.89	0.93
		0.89	0.93
	Average:	0.89 ± 0.02	0.95 ± 0.04

G.C. Column: 15% Carbowax 20M on 80/100 mesh Supelcoport
6 ft. x 1/4 in. o.d. glass
Temperature: Isothermal 60°C
Carrier Gas: Helium 30.3 ml/min.
MEK Retention Time: 1.25 minutes

TABLE VII

COMPARISON OF DESORPTION EFFICIENCIES OF MEK

Vapor Spike	Liquid Spike
0.92	0.91
0.92	0.92
0.89	0.92
0.91	0.92
0.92	0.92
Average: 0.91 ± 0.01	Average: 0.92 ± 0.004

3M 111103

TABLE VIII

EFFECT OF TIME ON DESORPTION EFFICIENCY OF MEK

Adsorption Time (Hrs)	Desorption Efficiency	
	Vapor State Spike Method	Liquid Spike Method
0.5	0.91	0.94
1.0	0.90	0.92
4.0	0.92	0.91
24.0	0.90	0.91

FIGURE 1a

3M 111105

FIGURE 15

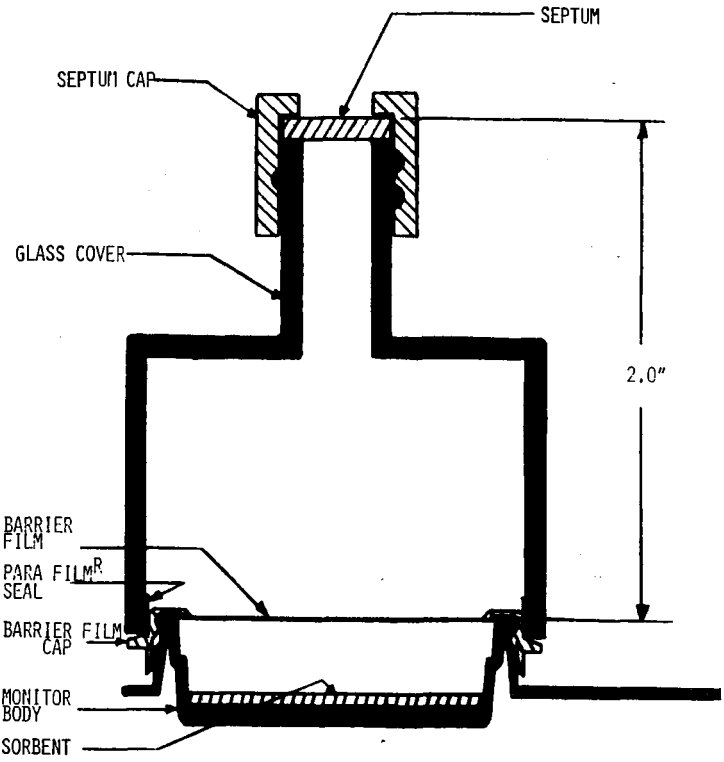

FIGURE 2

3M 111107