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.

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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.

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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.

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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.

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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.

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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.

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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.

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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.

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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.

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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.

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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.

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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.

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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.

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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.

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

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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.

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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

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

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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.

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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.

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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.

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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

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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.

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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.

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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.

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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.

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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

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.

3M 110429

Humidity
(Toluene)

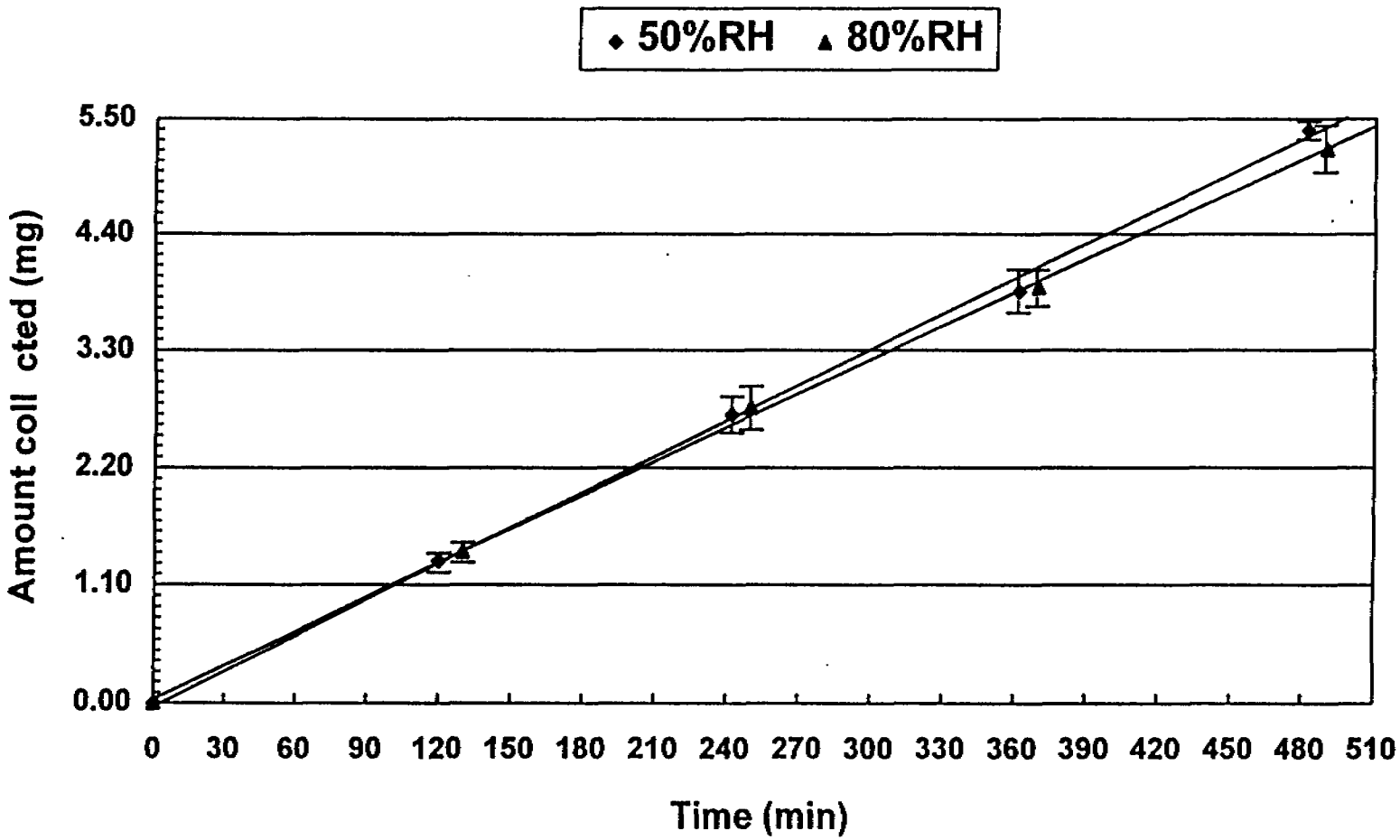
Relative Humidity (%)	2 Hour Sample (SR)	4 Hour Sample (SR)	6 Hour Sample (SR)	8 Hour Sample (SR)
50	1 30.8 ± 1.1	2 31.0 ± 1.5	3 29.7 ± 1.4	4 31.2 ± .3
80	5 30.4 ± 1.1	6 30.8 ± 2.3	7 29.4 ± 1.0	8 29.7 ± 1.4

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

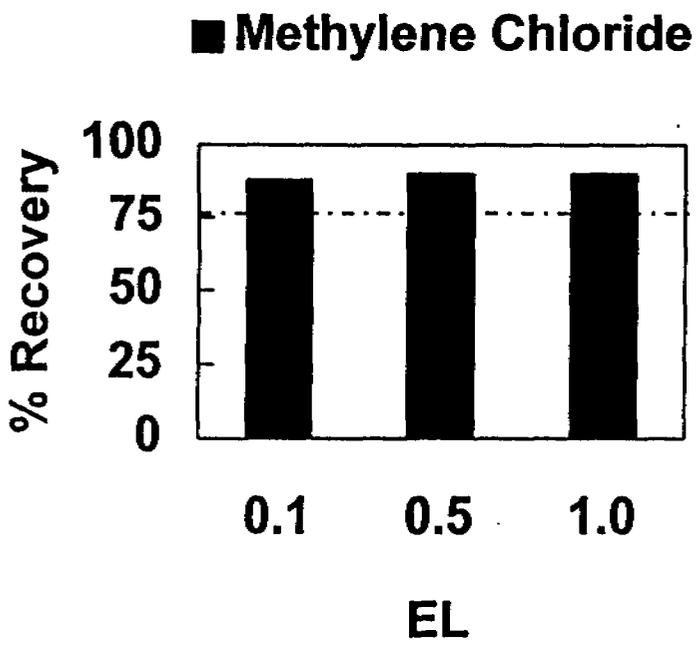
Accuracy = 2 CV ± Bias

Published SR = 31.4 cc/min.

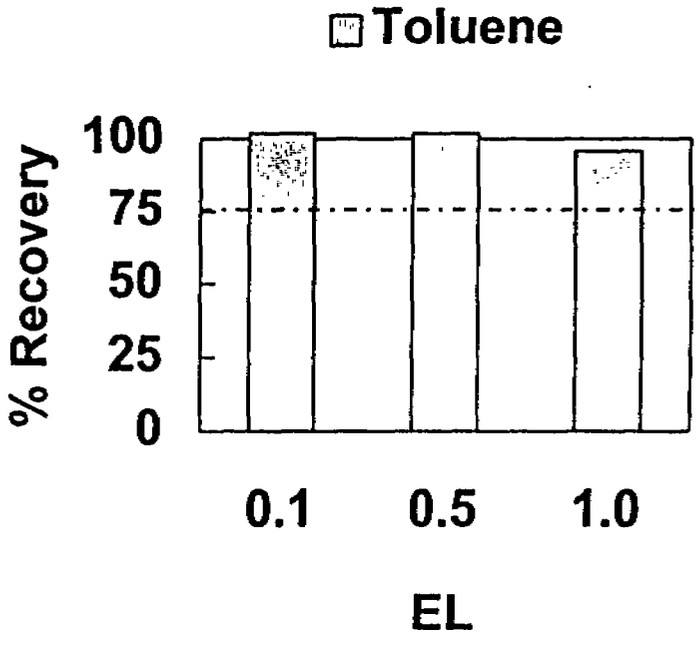
Temperature

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

Desorption Efficiency



1 EL: ~25ppm/8hrs



1 EL: 100ppm/8hrs

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.