SOLID SORBENT SAMPLING AND ANALYTICAL METHODS

David G. Taylor, Ph.D.
NIOSH
4676 Columbia Parkway
Cincinnati, OH 45226

I. Introduction

A. WWI gas mask research

B. W. A. Cook - late 20's and 30's; State of Connecticut

C. Last 20 years

1. Scattered use

2. Popularization

3. Wide interest

As far back as the 1930's, industrial hygiene solid sorbent sampling techniques were being employed. The development of these early methods grew out of the gas mask research of World War I and the subsequent application of solid adsorbents in industrial operations. One of the early industrial hygiene pioneers was Warren A. Cook who wanted to use activated carbon to collect benzene and other solvent samples in workroom atmospheres. The high temperature needed to strip the benzene from the charcoal, however, decomposed the solvent. So he and Ficklen developed the technique of freezing out the benzene from air samples passed through glass beads in a Pyrex U-tube cooled with dry ice. Upon moderate heating of the U-tube in the laboratory, the vaporized benzene was passed into a liquid and measured chemically. Since the chemical technique was complicated, Cook and Coleman developed a gravimetric procedure whereby the charcoal tube was weighed before and after sampling a known volume of air in order to estimate the solvent concentration. This technique was used for a large variety of solvents. However, specificity became a problem as industrial processes used more multiple solvent systems. The development of the gas chromatography in the fifties led to the present

broad application of solid sorbents to the sampling and analysis of multicomponent organic solvent samples. The missing links in Cook's industrial hygiene solid sorbent efforts were the ability to remove, intact, the substances of interest and the component separation capabilities of gas chromatography.

REFERENCES:

1. Cook, W.A. and J.B. Ficklen. "The Determination of Benzene in Air," J. Indus. Hyg., 17:41 (1935).

2. Cook, W.A. and A.L. Coleman. "Determination of Injurious Constituents in Industrial Atmospheres. II. Determination of Solvent Vapors in Air by Means of Activated Charcoal," J. Indus. Hyg., 18:194 (1936).

II. Advantages and Disadvantages of Sorbent Sampling

A. Gives TWA exposure information

B. Small, simple sampler

C. Easy handling and shipment

D. Can sample several compounds simultaneously

E. Personal pump costs

F. Not direct-reading

G. Sorbents do not collect particulates efficiently

III. Solid Sorbent Systems

A. Active Personal Samplers

1. Specific sorbent in tube

2. Personal sampling pump

3. Desorbing system - liquid or heat

B. Passive Monitoring Badge Systems

1. Diffusion badges

a. Draft shield

b. Air diffusion region

c. Sorbent

2. Permeation badges

a. Specific, individually-calibrated membrane

b. Sorbent

3. Desorbing system

C. Analytical Measurement

IV. Developmental Testing and Quality Assurance

A. Breakthrough of primary absorber

B. Lot-to-lot variations

C. Desorption efficiency

D. Humidity effect

E. Migration/stability

F. Derivatization sampling for unstable substances

G. Volatility, bed size and flow rate

V. Theory and Practice of Badge Sampling

A. Fick's law of diffusion

B. Adjusting sensitivity (exposure area)

C. Calibration (diffusion vs. permeation)

D. Interferences (membrane exclusion)

E. Integrity of sample

1. Capacity

2. Stability

F. Tampering with badge during sampling

G. Sources of badge information

VI. Testing Active Sorbent Methods - Vinyl Chloride example

VII. The Environmental Monitoring Process

The steps in this process and their possible effects on the analytical results are listed.

VIII. Vapor/Particulate Sorbent Sampling

A. Need for S/A systems

B. Method evaluation difficulties

1. Generation of simulation atmospheres

2. Need for new sampler

C. Defining V/P mixtures

D. Oxalic acid example

IX. Sources of Sorbent Information

A. Reference list

B. Sorbent sampling equipment

C. NIOSH methods available

THE ENVIRONMENTAL MONITORING PROCESS

Monitoring for airborne environmental contaminants is a specialized example of traditional analytical chemistry. This field is more specialized because traditional analytical chemistry has ignored the problems involved in air sampling and the large effect it has on the final results. As one example of the environmental monitoring field, let's consider the use of solid sorbent sampling and analysis to determine the exposure to workers to toxic chemicals in an industrial plant. Skin absorption and ingestion may play a role but inhalation is the primary route of exposure considered here.

I have indicated the steps of the entire monitoring process and listed at each step analytical items which may affect the results of the calculated air exposure level. Understanding these items will give an appreciation of how activities and actions taken during a monitoring survey affect the final analytical results.

1. PROBLEM (as presented to industrial hygienist)

   Knowing or learning about the problem in the plant, the industrial hygienist must redefine the problem as he interprets the facts. Consultation with the chemist may alter his plan of what substances may be important and should be sampled.

2. METHOD SELECTION

   This should be done in consultation with the laboratory. The concentrations expected, the interferences present and what other substances need to be monitored play a role in the selection.

3. SAMPLING STRATEGY

   a. The strategy is used to get a <u>representative</u> sample to determine the individual's exposure.

   b. Considerations which affect the desired result

      -- The work cycle

      -- The industrial process cycle

      -- Worker classifications

      -- Area vs. personal monitoring

      -- TWA vs. ceiling standards

-- Duration of sampling

-- Number of samples

4. SAMPLING

   a. Calibrated equipment

   b. Overloading or underloading (high concentration of contaminants or below analyte detection limit)

   c. Humidity (Toluene gives a 50% reduction in collection capacity at high relative humidity (80% vs. 7% RH))

   d. Appropriate flow and volume

   e. Collection efficiency (gases, aerosols, vapor/particulate mixtures)

   f. Sample ID and other information

5. SHIPPING SAMPLES TO LAB

   a. DOT regulations for shipping hazardous chemicals (e.g., bulk samples)

   b. Loss and breakage (less for sorbent tubes than bubblers)

   c. Stability

      -- Migration (VCM will equilibrate between two sections of charcoal in the same tube giving a false indication of breakthrough)

      -- Decomposition (MEK, cyclohexane on charcoal)

6. SAMPLE STORAGE

   a. Refrigeration, separate from bulk samples

   b. Stability (many substances are unstable, especially if sampled on the wrong sorbent)

      -- Oxidation (dry charcoal)

      -- Plating out on container

      -- Migration

7. ANALYSIS

   a. Recovery or desorption efficiency

   b. Positive or negative interferences; blanks

   c. Identification by specific detection methods

   d. Detection and detection limit (samples with undetected analytes should be reported as "less than")

   e. Calibration of lab instruments

8. REPORTING RESULTS

   a. Corrections for actual volume sampled

      -- Temperature and pressure (if different from pump calibration conditions)

   b. Corrections to mass of contaminant

      -- Collection efficiency, recovery or DE

      -- Conversion efficiency (e.g., ozone by KI methods)

   c. Calculation of air concentration

      -- mg/m^3 (particulates or gases) or ppm (gases and vapors only)

   d. Give method used and any problems (e.g., interferences which may have influenced result, samples that were unacceptable)

   e. Present facts, not opinions and do not give numerical results if the data is questionable. All numerical results tend to be used by others as absolute facts. All analytical results are <u>estimates</u> of exposure, not necessarily the absolute fact.

VARIABLES THAT AFFECT MONITORING DATA

1. Variables Affecting Accuracy of Air Sampling

   a. Collection Efficiency

      (1) Flowrate through sampler
      (2) Physical state of substance(s)
      (3) Samples capacity
      (4) Site competition on sorbent
      (5) Migration off sorbent

   b. Sample Stability

      (1) Vaporization
      (2) Reaction with media or other chemicals collected in sample
      (3) Catalytic decomposition

   c. Quantitative or reproducable recovery from samples

   d. Accuracy of sampling pump calibration or badge calibration

2. Variables Affecting Desorption Efficiency

   a. Technique used (thermal, liquid, and type, addition)
   b. Sorbent used
   c. Lot or variation in type of sorbent
   d. Loading of analyte on sorbent
   e. Presence and amount of coadsorbed contaminants
   f. Volume of eluent/sorbent
   g. Time of desorption
   h. Temperature of desorption

3. Variables Affecting Sorbent Capacity

   a. Type of sorbent
   b. Amount of sorbent
   c. Flow through sampler
   d. Presence of cocontaminants
   e. Total contaminant concentration
   f. Sampling time (c.f. breakthrough)
   g. Ambient temperature during sampling
   h. Ambient humidity during sampling

4. Variables Affecting Sample Stability on Sorbents

   a. Sorbent used
   b. Inherent chemical stability of analyte
   c. Cocontaminants on sorbent
   d. Storage temperature
   e. Volatility of analyte on sorbents
   f. Light sensitivity of analyte

TESTING ACTIVE SORBENT METHODS
-- An Example --

This is an example of the factors involved in sorbent methods development and how these factors can affect the accuracy of the reported results of a field survey using the method. If the laboratory developing the method has done a good job, many of the potential problems are minimized by the limitations stated in the final method. Vinyl chloride monitoring methods are used in this example. Not all of the problems encountered here would be expected for most compounds, but they illustrate the range of possible problems.

Selection of Sorbent Sampler

Ideally, you want a sorbent that quantitatively adsorbs the chemical during sampling, holds it during storage and releases all of it unchanged for analysis. In practice we can accept a method that collects all the material and releases a fixed fraction with no storage problem.

1. Activated coconut charcoal is one of the few sorbents with the collection capacity necessary. The 5% breakthrough volumes show this:

100 mg Sorbent	Breakthrough Volume (L)
Chromosorb 106	< 0.1
Tenax-GC	< 0.1
Silica Gel	< 0.1
Molecular Seive, 5A	2.0
Petroleum Charcoal, SKC-104	7.7
Coal Charcoal, BPL	8.2
Coconut Charcoal, MSA-6	10.3
Coconut Charcoal, SKC-105	10.6
Coconut Charcoal, PCB	8.1

Note that the capacity of the different lots of coconut charcoal can vary. In addition, larger tubes will improve the sampler capacity (up to 1 gram).

2. Flowrate affects the breakthrough volume (at a VCM concentration of 500 µg/L).

Rate (Lpm)	Volume (L)
1.0	0.9
0.2	2.4
0.05	5.2

Sample slowly (but not less than 5-10 mL/m) to get better adsorption and/or use larger sorbent beds.

3. Air concentration affects breakthrough (at 0.2 Lpm).

Concentration (µg/L)	Volume (L)
500 (∿200 ppm)	2.4
130	3.4
6.5	5.7

4. High relative humidity does not reduce the sorbent capacity for badge sampling (VCM) but for other substances this may be a factor.

5. Desorption efficiency should be greater than 80% and constant over the expected loading range for a given lot of sorbent.

Sorbent	DE Range (%)
MSA-6	80-90
PCB	93-101

Since these ranges came from different laboratories, this may be an interlaboratory effect indicating the need to do your own DE determinations.

6. Due to the volatility of VCM and heat generated during desorption, the method of desorption is important.

   a. Add carbon to cold CS_2 to minimize loss of VCM due to heat generated during desorption.

   b. Have a minimum headspace because the VCM will distribute itself between the air above the CS_2 (headspace) and the CS_2 itself (Henry's Law). One gets about 6% of VCM in a 1.5 mL headspace.

7. Migration of VCM from front to back s ction during storage occurs. This distribution takes only about one week at room temperature. At -20°C no migration occurs in at least three weeks. If only a single-section tube is used, then you would never know if losses had occurred during sampling. The known capacity of the sorbent usually is not reliable when many other substances are present. Thus, the two-section tube is preferable with proper (low temperature) storage.

8. Thermal desorption has been recommended. However, others have shown that if ethylene dichloride is present on the sampler, it will decompose (dehydrohalogenate) to HCl and VCM on charcoal. This would give false positive results (100% in the badge; Nelms reference below). Liquid desorption is preferred.

9. The sorbent mesh size and tube geometry affect the pressure drop and determine whether the personal sampling pump will work over the required period (up to 8 hours).

10. The VCM can be lost if the charcoal is transferred to vials with Polyseal caps. Apparently, this polymer absorbs VCM.

11. Finally, for badges there was no temperature effect for VCM (0-40° C). For other permeation badges, there was an effect (SO_2 negative, CO large positive).

The above examples suggest that many variables affect the results and must be controlled during sampling, storage and analysis. Written methods must take into account these factors.

See VCM method references:

J. E. Cuddeback et al., ES&T, 9, 1168 (1975).
R. H. Hill et al., Anal. Chem., 48, 1395 (1976).
S. A. Myers et al., AIHAJ, 36, 332 (1975).
L. H. Nelms et al., ibid, 49, 994 (1977).
L. W. Severs et al., ibid, 36, 669 (1975).

THEORETICAL BASIS OF BADGE SAMPLERS

A. Diffusion-controlled badges

Fick's first law of diffusion describes the rate of movement of gases through a fluid medium such as air.

$$J = - \frac{DA}{L} (C - C_o)$$

where J = the mass flux $(\text{moles/sec})_2$
D = diffusion coefficient (cm^2/sec)
A = area of badge opening (cm^2)
L = distance between badge opening and the internal collector (cm)
C = ambient concentration (moles/cm^2)
C_o = air concentration at collector surface (zero, if collector is adsorbing all of the gas)

The mass absorbed (M) is given by:

$$M = \frac{DA}{L} Ct$$

where $M = Jt$

Since the badge geometry $(\frac{A}{L})$ is fixed, the badge can be calibrated by exposing it to a known concentration for a given period of time to calculate the diffusion coefficient. This constant can be used with any badge of the same geometry.

B. Permeation-controlled badges

In these badges, the gas or vapor must pass through a membrane before being adsorbed onto the sorbent. The substance dissolves in the membrane, permeates to the other side (since there is a lower concentration there) and is adsorbed by the sorbent just inside the membrane. The calibration formula is:

$$C = \frac{MK}{t}$$

where K = permeation constant.

This formula can be derived from Fick's law above. One disadvantage is that this "K" cannot be used for similar badges. It is specific for that membrane and, thus, each badge must be calibrated separately.

PASSIVE MONITORS FOR PERSONAL SAMPLING
- Examples -

Name	Analyte(s)	Reference
Gas Badge	Organic vapors, NO_2, SO_2	Abcor Development Corp. Wilmington, MA
Organic Vapor Monitor	Organic vapors	3M Co. St. Paul, MN
3M - Hg	Hg	3M Co. St. Paul, MN
DuPont	Organic vapors	DuPont Co. E. B. Kring (215) 444-4188
Minimonitor	Vinyl chloride, SO_2, Cl_2, Alkyl Pb	REAL Inc. ES&T, 7, 526 (1973) AIHAJ, 39, 645 (1978)
Army - NH_3	NH_3	AIHAJ, 39, 749 (1978)
GE - CO	CO Electrochem, direct-reading	General Electric Co. Schenectady, NY
Palmes	NO_2, SO_2	AIHAJ, p. 579 (1976)
Alkylating agents	β-propiolactone	Arch. Envr. Health, 33(1), 33 (1978)
Univ. of Toronto	NO	Anal. Chem., 49, 1672 (1977) ibid, 50, 1871 (1978)

BADGE SAMPLING INFORMATION

1. Assumptions and Limitations of Diffusion Badges
   a. Constant exposure area and diffusion distance
   b. Quiescent diffusion zone (Steady-State)
   c. Complete retention of analyte
   d. Diffusion constant independent of concentration
   e. Fast response time
   f. Cannot sample particulates
   g. Minimum face velocity
   h. Precision, accuracy, and cost
2. Assumptions and Limitations of Permeation Badges
   a. Constant area and diffusion of concentration
   b. Permeation constant independent of concentration
   c. Complete retention of analyte
   d. Fast response time
   e. Individual calibration required
   f. Membrane integrity and aging
   g. Cannot sample particulates
   h. Minimum face velocity
   i. Precision, accuracy and cost
3. Advantage of Passive Monitors
   a. Advantages
      (1) No personal pump required
      (2) Worker acceptance of sampler
      (3) Integrated exposure for individual worker
      (4) Multisubstance collection

(5) Non-liquid, rugged sampler
(6) Easy use and shipment to laboratory
(7) Cost (?)

b. Disadvantages

(1) Results obtained at later time
(2) Cannot sample particulates
(3) High humidity and concentration may affect capacity
(4) No back-up section to check for sample loss
(5) Accuracy, Cost (?)

4. Comparative Testing of Three Organic Passive Monitors and the Charcoal Tube (CT)

Monitor	Toluene Concentration(ppm)		Vinyl Chloride Concentration(ppm)		
CT	15	208	0.14	1.0	2.6
A	15	202	0.13*	0.2*	2.5*
B	15	214	ND	1.2*	1.0*
C	19*	198	0.17	1.0	2.4

.03 .2 .5
ND .2 1.0

*Significantly different from CT result
Charcoal tubes used critical orifices
Conditions: 25°C; 80% RH; 100 FPM; 7 h sample time.

5. Evaluation of Mercury Vapor Passive Monitor*

Condition	Mean Concentration (mg/m^3) Instrument	3m Monitor
Hg Vapor	0.028	0.027
	0.120	0.130
	0.298	0.288
Hg Vapor + Cl_2	0.036	0.022
Hg Vapor + H_2S and SO_2	0.168	0.140

* From McCammon and Woodfin, A.I.H.A. J, August(1977)

Taylor says use badges in areas where contaminants are well known, after they have been checked out.

SAMPLING OF VAPOR-PARTICULATE MIXTURES

In recent years, there has been an increased effort placed on the monitoring of airborne substances in the workplace. This effort has included not only close coordination of the sampling and the analytical phases of monitoring, but also has involved the improvement in the efficiency of collection of gases and vapors in some samplers and particulate substances in other samplers. The traditional liquid impinger has some ability to collect both aerosols and vapors simultaneously, but the collection efficiency can be low. Moreover, the use of the midget impinger to collect personal air samples for monitoring exposure to organic substances has been largely supplanted in recent years by tubes containing sorbent materials such as activated charcoal. Since the solid sorbent tubes are easier to handle, there is less sample loss and more freedom of movement by the worker being monitored.

For substances that exist in workplace air as both particulate and vapor, the impinger was deemed an adequate sampling device. However, the newer solid sorbent tubes and passive monitoring badges are designed to efficiently sample gases and vapors but not particulates. Ortiz et al. tested the charcoal tube for penetration by aerosols (Ortiz, L.W., Ci.I. Fairchild, M.I. Tillery and H.J. Ettinger, "Aerosol Research and Development Related to Health Hazard Analysis - July 1, 1975 - June 30, 1976," Progress Report LA-5639-PR, Los Alamos Scientific Laboratory, Los Alamos, NM 1976). They found that the charcoal in a 150-mg tube collected about 21% of mono- and poly-disperse aerosols while the upstream glass fiber plug retained an average of 70% of the particulate. This would imply that the charcoal tube samples could collect vapors as well as at least 95% of the airborne particulates. On the other hand, the variability of aerosol penetration was large, about 55% relative standard deviation. This level of precision is unacceptable for personal monitoring, particularly for compliance monitoring, because the results of many samples could be in error by more than 100%.

Many solid or liquid substances are dispersed in the workplace as aerosols. These substances may also have enough vapor pressure to partially vaporize giving a mixture of particles and vapor. Samplers used to collect these substances must be able to collect both fractions efficiently. Developing and validating these sampling and analytical methods requires extra care.

Recent work has centered around a collection train consisting of a particulate filter followed by a solid sorbent tube. These types of sampling trains need to be evaluated and made available for sampling vapor-particulate mixtures.

1. Do you need to monitor for these substances?

   Acrylamide; aldrin; 4-aminobiphenyl; 2-aminopyridine; benzidine; biphenyl; cresols; 2,6-Di-t-butyl-p-cresol (DBPC, BHT); dichlorvos (DDVP); dinitrobenzene; dinitro-o-cresol (DNOC); dinitrotoluene (DNT); halowaxes: pentachloronaphthalene, tetrachloronaphthalene, trichloronaphthalene; hexamethylenetetramine (HMTA, Methenamine); hydroquinone; kepone; 4,4'-methylenebis (2-chloroaniline) (MOCA); p-nitroaniline; 4-nitrobiphenyl; oxalic acid; pentachlorophenol (PCP); p-phenylene diamine; phthalic anhydride; picric acid; polychlorinated biphenyls (PCB's)

   Then you probably need TWO-STAGE SAMPLING TRAINS!

2. How do you know if you have a vapor-particulate mixture?

   a. Odor of substance - a possible indicator

   b. Literature

   c. Calculation of Equilibrium Vapor Concentration (EVC)

   $$EVC = \frac{VP(mm\ Hg) \cdot MW \cdot 10^6}{760 \cdot 24.47}\ mg/m^3\ @\ 25^oC$$

   d. Presumptive test (compare EVC to OSHA standard)

   If $\frac{EVC}{Std}$ = 0.05 to 100-300, may have a mixture in the air.

   e. Confirming test

   Use dual sampling train in field (e.g., filter followed by bubbler in series).

   NOTE: (1) spiking filter, drawing air through it and checking for vapor losses, or (2) generating particulates in laboratory by the spray/dry technique may be unreliable tests.

3. Examples of vapor-particulate mixtures

Substance	Melting Point (°C)	Vapor Pressure (mm Hg)*	Equil. Vapor Conc. (mg/m^3)	OSHA Std. (mg/m^3)
Aldrin	90-101	6×10^{-6}	0.12	0.25
Dinitrobenzene	118	$\sim 4 \times 10^{-5}$	0.36	1.0
Hydroquinone	170.5	1.87×10^{-5}	0.11	2.0
MOCA	99-107	4.5×10^{-6}	0.06	
Oxalic acid	101	2.3×10^{-4}	1.6	1.0
PCB's (Aroclor 1242)	41-79	$\sim 2 \times 10^{-4}$	2.8	1.0
Pentachlorophenol	191	$\sim 2.7 \times 10^{-4}$	3.9	0.5
Phthalic anhydride	131	$5\text{-}6 \times 10^{-4}$	3.5-4.5	12.0

*At 25°C

4. Operating deficiencies in samplers designed for gases and vapors when used for vapor-particulate atmosphere (examples: bubblers, solid sorbent tubes, passive monitor badges).

   a. Expect low results due to poor collection efficiency of particulates.

   b. Expect variable results on replicate samples using charcoal tubes.

   c. Sampling two areas having the same concentration of material but at different temperatures will give unequal results, since the vapor fraction varies considerably with temperature.

5. Oxalic acid - a case study

   a. Solid, with melting point = 101°C and molecular weight = 126.1

   b. Could not find vapor pressure data initially.

c. Developed analytical method

1. GC-FID derivatization (TMS ester)

2. PTFE filters compatible with analytical method

d. Tested for vapor by spiking

Collected particles from generated concentration and then drew clean air through that filter. Found no weight losses from filter after drawing air through and concluded that no vapor was present.

e. Generation

1. Spray/dry atomization from aqueous solution

2. Particle size checked with Andersen impactor

3. Collection efficiency using a backup filter was found to be 99.6%

f. Sample storage

1. 54% loss in three days; 100% in seven days

2. All found on filter backup pad - first indication of vapor

g. Further test for vapor

Dry N_2 passing through solid in tower picked up vapor

h. Referral to literature gave vapor pressure data

Pure oxalic acid VP = 2.3×10^{-4} mm Hg

(Dihydrate = 2.65 mm Hg)

Equilibrium vapor concentration = 1.56 mg/m^3 ($1.8 \times 10^{+4}$ mg/m^3 for dihydrate)

OSHA permissible exposure limit = 1.0 mg/m^3

Thus, expect at equilibrium to have all vapor at the PEL.

Sh uld use dual particulate/vapor sampler in field since any airborne particulate is not at equilibrium with its vapor in the air.

6. Ways to minimize development problems

   a. Know the physical form of the substance in the air

   b. Know what is being generated in the laboratory. Avoid spray/dry generation of aerosols when vapors are likely to be present.

   c. Avoid spiking tests to check for vapor losses from aerosols on filters

   d. Test sampler in field side-by-side with independent method

   e. Do filter collection efficiency testing at <u>low</u> end of concentration range.

   f. Check sample stability

   g. Use a dual sampler when a vapor-particulate mixture is possible.

SELECTED SOLID SORBENT REFERENCES

January, 1975 - December, 1979

The following references are for sampling and analytical methods using solid sorbent samplers. Most are active samplers (tubes); some are for passive samplers (badges using no pump). Only American Industrial Hygiene Association Journal (AI) and Analytical Chemistry (AC) references are included. Certainly, good information can be found in other journals, but this selection will give some idea of the scope of the field.

1975 (AI - Vol. 36)

1. "The Use of Activated Carbon for Sampling Industrial Environs," p. 278.

2. "Determination of Vinyl Chloride Monomer at the Sub-ppm Level Using a Personal Monitor," p. 332.

3. "Personal Air Sampling for Vapors of Aniline Compounds," p. 538.

4. "A Charcoal Sampling Method and a Gas Chromatographic Analytical Procedure for Carbon Disulfide," p. 618.

5. "Monitoring Personnel Exposure to Vinyl Chloride, Vinylidene Chloride and Methyl Chloride in an Industrial Work Environment," p. 669.

1976 (AI - Vol. 37; AC - Vol. 48)

1. "Evaluation of Charcoal Sampling Tubes," AI, p. 37.

2. "A Simple Gas Chromatographic Method for the Analysis of Trace Organics in Ambient Air," AI, p. 165.

3. "Respirator Cartridge Efficiency Studies: VI. Effect of Concentration," AI, p. 205.

4. "The NIOSH Charcoal Tube and Other Solid Sorbent Sampling Tube Certification Program," AI, p. 489.

5. "Respirator Cartridge Efficiency Studies: VII. Summary and Conclusions," AI, p. 514 (see references in this paper for

earlier work). (These seven papers give alot of data on sorbent capacity and humidity effects.)

6. "Personal Sampler for Nitrogen Dioxide," AI, p. 570

7. "Determination of Trace Hazardous Organic Vapor Pollutants in Ambient Atmospheres by Gas Chromatography/Mass Spectrometry/Computer," AC, p. 803.

8. "Gas Chromatographic Determination of Vinyl Chloride in Air Samples Collected on Charcoal," AC, p. 1395.

1977 (AI - Vol. 38; AC - Vol. 49)

1. "A Relation Between Heat of Adsorption and Breakthrough Time for Low Concentrations of Organic Vapors in Air Passing a Bed of Charcoal at Room Temperature," AI, p. 46.

2. "Desorption of Organic Solvents from Charcoal Collection Tubes," AI, p. 144.

3. "Improvements in the Validity of Charcoal Tube Sampling by the Use of a Unique Low Flow True Total Volume Sampling Pump," AI, p. 195.

4. "The Filtration Efficiency of Organic Vapor Sampling Tubes Against Particulates," AI, p. 277.

5. "A Solid Sorbent Personal Sampling Method for the Simultaneous Collection of NO_2 and NO in Air," AI, p. 359.

6. "A New Personal Dosimeter for the Monitoring of Industrial Pollutants," AI, p. 371.

7. "An Evaluation of a Passive Monitor for Mercury Vapor," AI, p. 378.

8. "Performance Testing of the NIOSH Charcoal Tube Technique for the Determination of Air Concentrations of Organic Vapors," AI, p. 476.

9. Collaborative Testing of a Gas Chromatographic Charcoal Tube Method for Seven Organic Solvents," AI, p. 543.

10. "A New Method for Monitoring Personal Exposure to Ethylene Oxide in the Occupational Environment," AI, p. 635.

11. "Field Air Sampling of Pesticide Vapors with Polyurethane Foam," AC, p. 7.

12. "Personal Vinyl Chloride Monitoring Device with Permeation Technique for Sampling, AC, p. 994.

1978 (AI - Vol. 39; AC - Vol. 50)

1. "Sampling and Analysis of 2,6-Di-t-butyl-p-cresol," AI, p. 78.

2. "Phase Equilibrium Method for Determination of Desorption Efficiencies," AI, p. 240.

3. "Dynamic U-Tube System for Solid Sorbent Air Sampling Method Development," AI, p. 321.

4. "Criteria for the Evaluation of Methods for the Collection of Organic Pollutants in Air Using Solid Sorbents," AI, p. 349.

5. "Sampling for Organic Chemicals in Workplace Atmospheres with Porous Polymer Beads," AI, p. 385.

6. "Solid Sorbent Sampler for White Phosphorous in Air," AI, p. 608.

7. "A Solid Sorbent Personal Sampling Method for the Determination of Acrolein in Air," AI, p. 615.

8. "Field Tests of a Permeation-Type Personal Monitor for Vinyl Chloride," AI, p. 645.

9. "Collection and Determination of Trace Amounts of Organo-Thiophosphates in Air Using XAD-2 Resin," AI, p. 678.

10. "A New Personal Sampler for Organic Vapors," AI, p. 701.

11. "Development and Evaluation of an Ammonia Dosimeter," AI, p. 749.

12. "Establishing a Protocol from Laboratory Studies to be Used in Field Sampling Operations," AI, p. 880.

13. "Analysis of Charcoal Tube Samples for Carbon Disulfide Using a Photoionization Detector," AI, p. 939.

14. "Sampling and Atomic Absorption Spectrometric Determination of Arsine at the 2 $\mu g/m^3$ Level," AC, p. 1094.

15. "Portable Device with XAD-4 Resin Trap for Sampling Airborne Residues of Some Organophosphorous Pesticides," AC, p. 1229.

16. "Solid Sorbent for Sampling Acrolein in Air," AC, p. 1839.

17. "Comparison of Porous Copolymers and Related Adsorbents for the Stripping of Low Molecular Weight Compounds from a Flowing Air Stream," AC, p. 1842.

18. "Mass Transfer Effects in a Nitric Oxide Dosimeter," AC, p. 1871.

1979 (AI - Vol. 40; AC - Vol. 51)

1. "Simplified Description of Adsorption Breakthrough Curves in Air Cleaning and Sampling Devices," AI, p. 169.

2. "Collaborative Study of Reference Vinyl Chloride Charcoal Tubes," AI, p. 200.

3. "Air Sampling and Analytical Method for 4,4'-Methylenebis(2-chloroaniline)," AC, p. 19.

4. "Determination of Airborne Organic Vapor Mixtures Using Charcoal Tubes," AI, p. 380.

5. "Field Comparison of Two Methods for the Determination of NO_2 Concentration in Air," AI, p. 437.

6. "Personal Samples for NOx," AI, p. 588.

7. "Sampling and Analysis of Acetic Anhydride in Air," AI, p. 803.

8. "A Sampling and Analytical Method for Vinylidene Chloride in Air," AI, p. 888.

9. "The Quantitative Determination of Acrylonitrile, Acetonitrile and Acetone in Workplace Air," AI, p. 904.

10. "Recovery of Acrylonitrile from Charcoal Tubes at Low Levels," AI, p. 923.

11. "Air Sampling and Analytical Procedures for Benzidine, 3,3'-Dichlorobenzidine and their Salts," AI, p. 970.

12. "Simultaneous Determination of Polar and Non-polar Solvents in Air Using a Two-Phase Desorption from Charcoal," AI, p. 1006.

13. "Total Elemental Content Passive Personal Monitors," AI, p. 1046.

14. "Modification of a Gas Chromatographic inlet for Thermal Desorption of Adsorbent-Filled Sampling Tubes," AC, p. 2333.

15. "Ohm's Law, Fick's Law, and Diffusion Samplers for Bases," AC, p. 2400.

SOURCES OF SOLID SORBENT SAMPLING EQUIPMENT

A. Pumps

Bendix Corporation
Environmental and Process
Instruments Division
P. O. Box 831
Lewisburg, WV 24901

DuPont Co. (Applied Technology)
1007 Market Street
Wilmington, DE 19898

MDA Scientific, Inc.
808 Busse Highway
Park Ridge, IL 60068
(312) 696-4250

Mine Safety Appliances Co.
Pittsburgh, PA 15208

Anatole J. Sipin Co.
425 Park Avenue, South
New York, NY 10016

SKC Inc.
R. D. 1
395 Valley View Road
Eighty Four, PA 15330
(412) 941-9701

Spectrix Corp.
3594 Haven Avenue
Redwood City, CA 94063

B. Sorbent Tubes

Mine Safety Appliances Co.
Pittsburgh, PA 15208

SKC Inc.
R. D. 1
395 Valley View Road
Eighty Four, PA 15330

Many other suppliers sell sorbents which have been used in sorbent tubes.

C. Badges

Abcor Development Corp.
850 Main Street
Wilmington, MA 01887

DuPont Co. (Applied Technology)
1007 Market Street
Wilmington, DE 19898

REAL Inc.
Box 3341
Baton Rouge, LA 70821

3M Co.(OH & SP Division)
3M Center, Building 220-7W
St. Paul, MN 55101

D. Thermal Desorber

Century Systems Corp.
P. O. Box 133
Arkansas City, KS 67005
(316) 447-3311

NIOSH MANUAL OF ANALYTICAL METHODS (FIVE VOLUMES)

The increased availability of methods using solid sorbent sampling devices is indicated in the following table. Now more than half of NIOSH personal sampling methods use sorbents.

Sampling Devices Used in NIOSH Methods

Device	Frequency (%)
Solid sorbent	52
Filter	29
Impinger or bubbler	12
Filter/bubbler or filter/solid sorbent series	6
Bag	1

Nearly all of the modern industrial hygiene methods use instrumental techniques for analysis. Spectrometry and gas chromatography coupled with a variety of detectors comprise 75% of the NIOSH methods as indicated in the table.

Analytical Techniques Used in NIOSH Methods

Technique	Frequency (%)
Gas chromatography	53
Atomic absorption spectrometry	11
Other spectrometric	11
HPLC	6
Other	19

Requests for the Manual should be directed to the Superintendent of Documents. The order information is below:

Volume No.	No. of Pages	GPO Order No.	Cost
1	807	017-033-00267-3	$ 8.75*
2	968	017-033-00260-6	9.75*
3	876	017-033-00261-4	9.00
4	528	017-033-00317-3	7.25
5	534	017-033-00349-1	9.00

Order from: Superintendent of Documents
U. S. Government Printing Office
Washington, DC 20402
(202) 783-3238 (Can use Visa or Master Card)

*These volumes are currently out-of-print at GPO, but they can be obtained from the National Technical Information Service, Springfield, VA 22161. Order Stock No. PB274-845 (Vol. 1), paper copy price $36.00; and stock No. PB276-624, (Vol. 2) $43.00; microfiche price $3.50.