INTER-OFFICE MEMO Olin

TO Lloyd Stakes AT Lake Charles DATE September 9, 1980

FROM D. B. Smith AT New Haven COPY TO L. A. Krause
N. Patel
C. Self

SUBJECT Guide To The Use Charcoal Tubes For Monitoring Airborne Organic Vapors

The use of glass tubes packed with activated carbon for the quantitative collection of airborne organic vapors is well documented throughout the industrial hygiene literature. Generalization of parameters influencing collection and desorption efficiencies have also been reported. An excellent review by Melcher et al appearing in the American Industrial Hygiene Association Journal (39) 5/78 page 349 is attached. Complete sampling and analytical methods for a number of single compounds and mixtures are abundently available. Many of these methods have been rigorously validated following the use of vapor generation systems and exhaustive field testing.

When monitoring for a new compound or a unique mixture it is imperative that the desorption efficiency be determined from tubes spiked with known amounts of compound. Collection efficiency can only be determined from the use a vapor generation system which produces known concentration of the compound(s) or by closely monitoring the breakthrough or backup section of a charcoal tube from an actual field sample. Generally, if the amount of analyte in the breakthrough section exceeds 25% of the main section the sample is declared invalid. Data from such a sample is often reported as "minimum concentration present". A reduction of sampling time and/or sampling rate will reduce breakthrough to within exceptable limits in most cases.

As we recently discussed there is a need to standardize how a charcoal tube is treated relative to our two laboratories to insure that desorption efficiencies are being determined in the same manner. Information contained in the following sections highlights some important aspects of charcoal tube technology.

The Charcoal Tube

Three sizes of charcoal tube are readily available commerically for the routine monitoring of a wide range of organic compounds. The tubes are generally packed with a coconut based charcoal and differ only by the amount of charcoal and tube dimensions. The volume of desorption solvent relative to the amount of charcoal can drastically effect desorption efficiency. The three types of common charcoal tubes and recommended desorption solvent volumes are described in Table I.

TABLE I

TUBE TYPE	MILLIGRAMS FRONT/REAR	MILLILITERS OF DESORPTION SOLVENT
Standard	100/50	1/1
Large	400/200	3/1
Jumbo	800/200	5/2

Desorption Solvent

The most commonly used desorption solvent used in conjuction with the charcoal tube and the FID detector is carbon disulfide (CS_2) owing to its minimal FID response. It is also a common practice to utilize solvent mixtures such as 95% CS_2 - 5% isopropanol to improve the desorption of moderately polar compounds. Other solvents such as hexane and dichloromethane are also used. The need to use a solvent mixture or an alternate to CS_2 is generally dictated by poor desorption efficiency ($< 50\%$) for a particular compound. The use of mixtures and alternate solvents can lead to analytical problems on the GC particularly if a large solvent peak masks components from the sample. An increase in desorption solvent volume may sometimes improve recovery with an attendent loss in sensitivity due to dilution of the sample.

Quality Control

The most valuable aid to establishing credibility relative to charcoal tube analysis is the routine use of spiked tubes and the attendent percent recovery of the analyte. Failure to achieve reproducible recovery may indicate an instrument malfunction or a calibration standard problem.

As a matter of routine spiked tubes prepared by a competent analyst or chemist must be analyzed along with each batch of field samples. Data from a routine analysis can be tabulated and evaluated statistically as it accumulates resulting in a wealth of information concerning the precision and accuracy of the analytical method.

Darrell B. Smith

DBS/gmm
Attachments

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A small tube containing a solid sorbent is convenient to use for collecting and concentrating trace organics in ambient air and worker breathing zones. Many techniques for air sampling with solid sorbents, especially for the long term eight hour sample, are relatively new. It is necessary to have criteria to judge methods utilizing these techniques and to establish guidelines which are accurate and practical. Parameters which affect collection and recovery and information necessary to define, develop and evaluate a sampling method are discussed. Progressive steps for the development and validation of air sampling methods are recommended.

Criteria for the evaluation of methods for the collection of organic pollutants in air using solid sorbents*

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introduction

In the early development of solid sorbent sampling techniques, a ten minute sample period was adequate to establish the concentration of a compound in air in an area. Since the sampling period was short, a large number of variables could be tested for the method validation in a relatively short time. Secondly, parameters such as humidity were not considered critical for short samples. Recently, the emphasis has been toward the development of portable personnel sampling systems which could be used up to eight hours to determine "time weighted average" (TWA) exposures.

Validation of methods for long term sampling becomes quite time consuming and more difficult since parameters such as humidity and flowrate are more critical. It is therefore also important to define the data necessary to validate a method in the most efficient manner. The main emphasis in this paper is on the collection of organic pollutants with solid sorbents followed by desorption with a suitable solvent and analysis. This includes a majority of the samples presently being collected and new methods being developed. Basic principles and specific parameters which can cause errors if not considered, are discussed.

Although the procedures discussed will be directed toward ambient air monitoring, either for industrial hygiene or air quality, adaptation can be made for monitoring stationary sources if particular attention is given to examining the extreme conditions often found in these situations.

With this scope in mind, the general areas discussed will be:

(1) Some of the parameters which affect collection and recovery, how the parameters can be evaluated, and what extrapolations can be made.
(2) What information is necessary to define and develop a tentative collection and recovery procedure.
(3) What criteria are necessary to evaluate a detailed validation of a tentative procedure which has been developed through an in-depth study or by extrapolation of a method for a similar compound.

analytical procedure

The total monitoring method can be divided into

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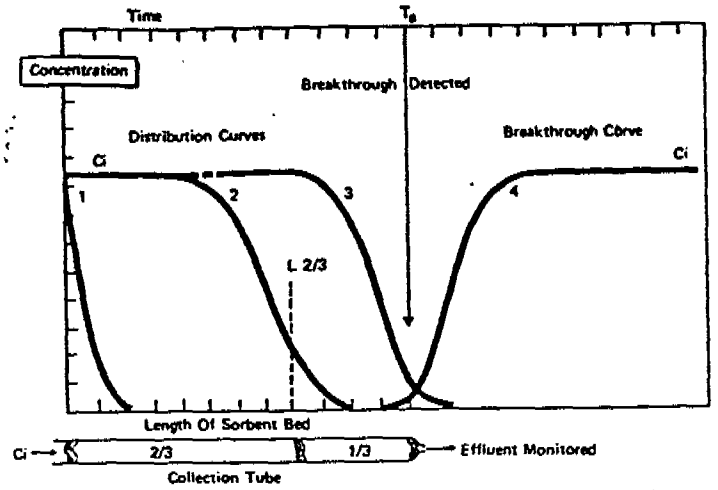

Figure 1 — Concentration distribution in a solid sorbent and vapor breakthrough.

the Analytical Procedure and the Sampling Procedure. If we define the Analytical Procedure as the determination of specific compounds in the desorption solvent, then either procedure can be changed independently as long as the interfacing parameters are considered. However, an adequate analytical procedure must be available before collection and recovery data can be obtained.

Gas chromatography is the most widely used analytical technique because of its selectivity and sensitivity. Gas chromatographic procedures are available or can be developed for a wide range of organic compounds by the proper selection of columns and detectors. The range can be broadened by using chemical derivatives and gas chromatographic/mass spectrometric techniques.

It is beyond the scope of this paper to discuss the complexities of the gas chromatographic or other analytical techniques; however, Table I lists analytical parameters which should be determined before and during the Sampling Procedure development. A general guide for industrial hygiene laboratory quality control has been prepared.[1]

TABLE I
Interfacing Analytical and Sampling Procedures

1. Sensitivity	sensitivity range compatible with amount of compound to be collected
2. Specificity	interferences in the area and on a broader scale investigated
3. Reproducibility of analysis	over concentration range to be studied
4. Reproducibility of apparatus	operating conditions well defined and columns, reagents etc. widely available
5. Adaptability	compatible with desorption solvents and other reagents
6. Simplicity	rapid, uncomplicated procedure
7. Automated	automatic injection and data handling systems

sampling procedure

The sampling procedure can be subdivided into collection and recovery, each of which involve a number of parameters which must be determined. In many cases, extrapolation of existing information serves as a guide to the selection of a suitable collection sorbent and desorption solvent. Although many of the parameters involved have been studied in detail, the number of variables encountered in field sampling are often too great to rely solely on these extrapolations for untested compounds. Verification of the collection and recovery in the laboratory before the samples are taken saves time and reduces errors.

Deteriorative effects on collection efficiency will be detected, after the fact, by high concentrations on the "back-up" section. However, if the factors are recognized before or during sampling, a greater safety factor can be applied to the sample volume which will reduce

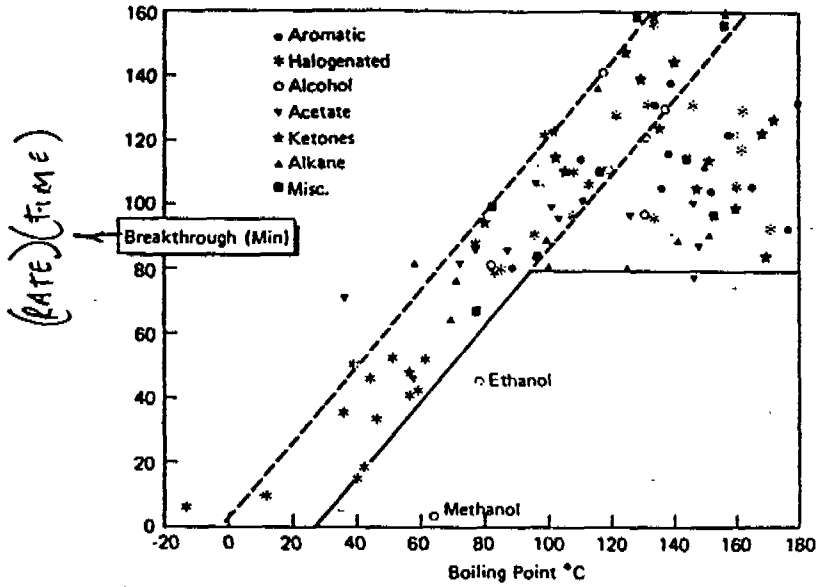

Figure 2 — Breakthrough of organic compounds through activated carbon respirator cartridges.

the number of invalid samples and the need to resample. Factors which cause changes in recovery are more insidious. Unless these are understood and can be related to the chemical and physical properties of the compounds collected, errors can go undetected.

collection

sorption process

Without getting too deeply in adsorption theory, we can look at what happens when air, containing an organic compound at concentration Ci, is pulled through a tube containing a solid sorbent. Figure 1 illustrates the distribution curve of the compound through the sorbent bed and the breakthrough curve of the compound in the effluent.

At the start of collection the compound is distributed through a section of the sorbent as shown by curve 1. After continued collection this section becomes "saturated" that is, an equilibrium is established with incoming concentration Ci where the vapor sorption and desorption rates are equal. This is shown by curve 2. The sorption front has moved through the front section of the collection tube (L 2/3) and is being collected on the backup section. If collection continues, the equilibrium zone lengthens and the compound begins to breakthrough the collection tube at time T_B, as shown by curve 3. The breakthrough curve 4 is generated by monitoring concentrations of the compound in the effluent, and when all the sorbent is "saturated" the effluent concentration approaches the input concentration Ci.

Breakthrough is defined as the detection of the compound in the effluent as a percentage of Ci. As a practical guide in air sampling this is often set at 5%.[2] The breakthrough volume, which is more indicative of the collection efficiency, is the product of the sampling rate and the sampling time. A more detailed discussion of the collection mechanism can be found in the literature for sorbents such as charcoal,[3-7] silica gel[8,9] and gas chromatographic packings.[10,11]

A general guideline can be proposed for actual field samples. If less than 10% of the total amount collected is found on the 1/3 backup section, significant loss of the compound has probably not occurred, and if greater than 25% is detected loss has probably occurred and results should be reported as "minimum amount present". More specific values can be obtained for this general statement by a detailed study of the breakthrough profiles for each specific sorbent and sorbate.

Factors which affect collection efficiency are discussed below. The degree to which each factor

contributes depends on the specific sorbent and sorbate.

properties of the compound

A number of equations have been developed to relate the properties of the compound to collection efficiencies.[3,6,9] Some equations become quite involved and often, require information not readily available for many compounds. It is usually more efficient to obtain experimental breakthrough data on a specific collection system for the compounds of interest. Correlation graphs can then be prepared for a group of compounds by plotting the breakthrough volume (or time) against a physical property. For example, experimental breakthrough data, or data from the literature,[6] can be plotted as shown in Figure 2. Up to a boiling point of 120°C, a very definite trend is observed. By relating the boiling point of an untested compound, some predictions can be made if the other factors discussed below are considered.

nature of sorbent

In selecting a sorbent for high collection efficiency, the recovery of the compound must also be considered. Often a mutual compromise may be necessary to obtain an acceptable system. Table II lists some of the most used sorbents and the types of compounds collected. Overlap allows some flexibility when sampling mixtures. By decreasing the sorbent size, the efficiency increases because of the increase in surface area;[7] however, the pressure drop also increases and limitations of the sampling pump must be considered. Prior treatment and activation of the sorbent will affect efficiencies. For example, not all types of charcoal are the same and not all batches of the same type charcoal necessarily have the same collection and recovery properties.[12-15]

size of collection tube

In general, if the size (amount of sorbent) is doubled the breakthrough volume is doubled. A somewhat greater increase in sampling time may be observed depending on the shape of the sorption zone front, as shown in Figure 1, since the sorbent is not at full capacity at the point of breakthrough.

flow rate

The effect of flow rate varies with the sorbent. In some cases once the optimum flow rate is reached no increase in breakthrough volume is observed with reduction in flow rate.[7] In other cases the efficiency continues to increase,[12,13] as shown in Figure 3. The coconut base carbon reached a maximum efficiency at approximately 100 ml/min. while Dow developmental adsorbent XF-4175L (Saran Carbon) continued to increase in efficiency. The linear velocity at optimum conditions should be an important

TABLE II
General Sorption-desorption Systems for Organic Compounds

Sorbent	Desorption Solvent	Types of Compounds
Activated carbon	Carbon disulfide, Methylene chloride, Ether (1% Methanol or 5% Isopropanol sometimes added)	Misc. volatile organics: Methyl chloride vinyl chloride and other chlorinated aliphatics, aliphatic and aromatic solvents, acetates, ketones, alcohols etc.
Silica gel	Methanol, Ethanol Diethyl ether, water	Polar compounds: alcohols, phenols, chlorophenols, chlorobenzenes, aliphatic and aromatic amines, etc.
Activated alumina	Water, Diethyl ether, Methanol	Polar compounds: alcohols, glycols, ketones, aldehydes, etc.
Porous polymers	Ether, Hexane, Carbon disulfide, Alcohols	Wide range of compounds: phenols, acidic and basic organics, multi-functional organics, etc.
Chemically bonded and other GC packings	Ether, Hexane, Methanol	Specialized: High boiling compounds pesticides, herbicides, polynuclear aromatics, etc.

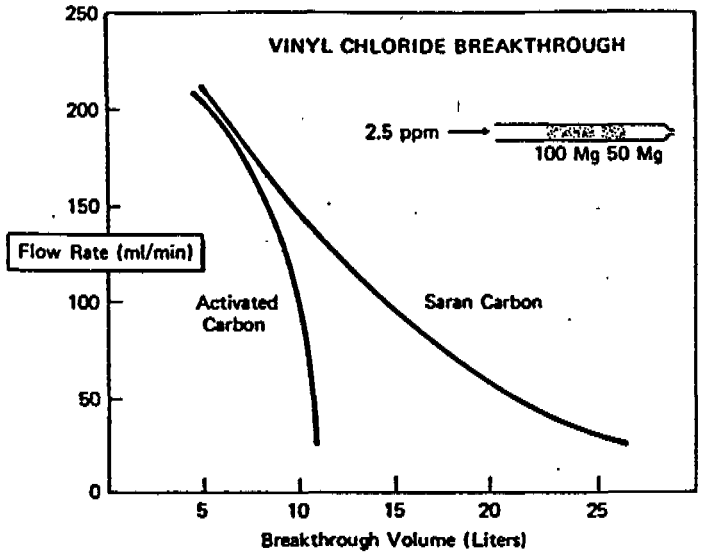

Figure 3 — Collection efficiency of activated coconut base carbon and Saran carbon for vinyl chloride.

consideration when extrapolating data to different size tubes.[16]

concentration

Breakthrough occurs sooner for higher concentrations. For charcoal the empirical Freundlich isotherm appears to apply.[6,13] This equation takes the form:

$$\log T_B = \log a + b \log c \qquad (1)$$

A straight line results if the log of the breakthrough time T_B is plotted against the log of the concentration, C. The line will have the slope b and intercept of log a, and is shown in Figure 4.

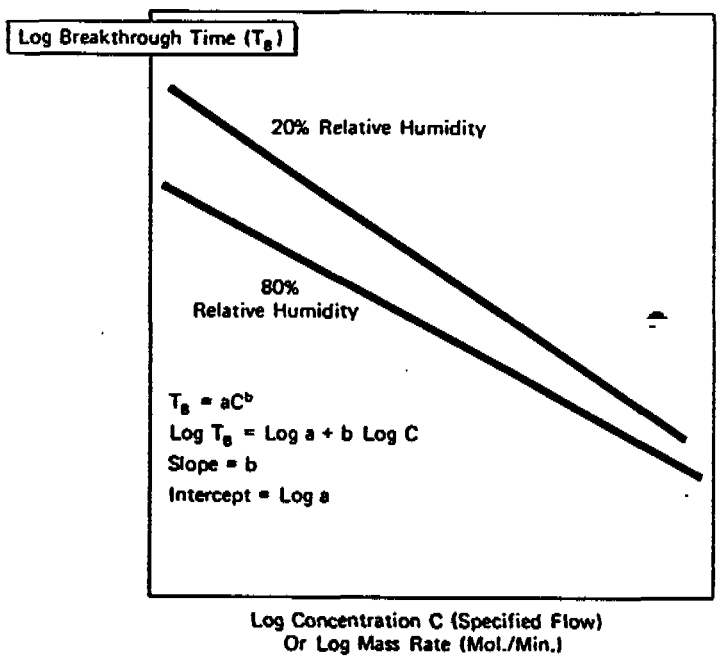

Figure 4 — Breakthrough time as a function of concentration.

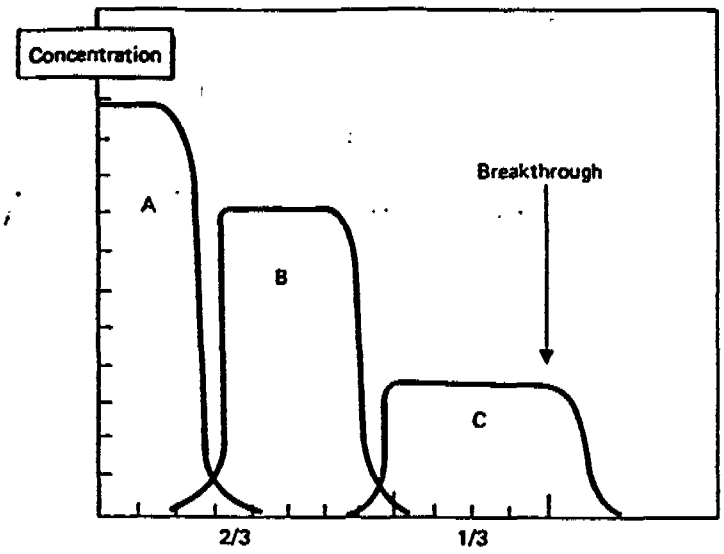

Figure 5 — Effect of Coadsorption on breakthrough.

Equations developed for the collection of amines on silica gel predict the amount of a compound collected is independent of the inlet concentration and flow rate.[9] A theoretical approach to the collection of compounds on gas chromatographic packings has also been reported.[10]

humidity

In general, an increase in humidity will result in an increase in breakthrough. The magnitude of this effect depends on the properties of the sorbent and sorbate. Although only a small amount of water is collected on charcoal the high ratio of water molecules to the compound of interest affects the sorption-desorption equilibrium and increases breakthrough as much as 50%.[14] A greater effect is observed for low concentrations of sorbate as indicated by the change in the slope for high humidities in Figure 4.

Polar sorbents such as silica gel and alumina, adsorb water more strongly than most organic compounds. This not only continues to reduce the effective length of the collection tube but also displaces compounds already collected. The extent of displacement is dependent on the polarity of the collected compounds. This effect can be treated in terms of coadsorption discussed next.

coadsorption

Figure 1 deals with the collection of one compound. When two or more compounds are collected, the compound most strongly held will displace the other compounds, in order, down the length of sorbent bed Figure 5. For a polar sorbent, compounds with the largest dielectric constant and dipole moment are most strongly held. For non-polar compounds, preferences are usually for the compounds of a higher boiling point or a larger molecular volume.[3]

temperature

An increase in temperature will result in an increase in breakthrough. There is little specific information available for the various sorbents. For charcoal a general guideline has been suggested that for every 10°C rise in temperature the breakthrough time will be reduced by 1-10%.[17]

migration

A false indication of breakthrough may be caused by migration of the compounds collected on the front section to the backup section over an extended storage period. This equilibration approaches 33.3% on the backup section for the more volatile compounds.[13,14] This problem can be reduced by refrigerating samples as soon as possible, or eliminated by separating the front and backup sections.

recovery

desorption efficiency

A number of factors influence recovery

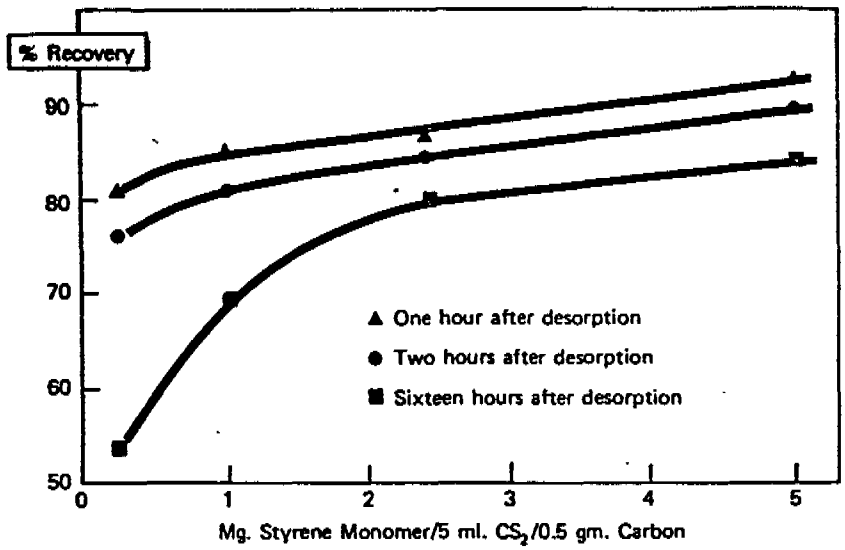

Figure 6 — Variation of desorption efficiency of styrene monomer with concentration and desorption time.

efficiencies (that fraction recovered of total compound collected when no breakthrough has occurred). The desorption efficiency is the most significant of the factors in defining the sorption-desorption system. Although desorption efficiency cannot always be isolated, it can be determined experimentally and is one of the first indicators of potential in a suggested method. Some of the sorption-desorption systems used are listed in Table I.

Although the desorption efficiency is generally treated empirically, some insights are obtained from a theoretical approach. A study has shown,[18] that for several types of compounds collected on charcoal, the system can be treated as a phase equilibrium. Preliminary data also indicates the same treatment can be applied to silica gel and porous polymers.[20,21] The organic compounds are partitioned between the solid adsorbent and the desorption solvent according to the equation:

$$\frac{1}{D} = K \frac{\text{mg sorbent}}{\text{mg solvent}} + 1 \qquad (2)$$

where D is the desorption efficiency expressed as a fraction and K is an equilibrium constant.

This concept is important since it indicates that the solvent - sorbent ratio cannot be changed without affecting the desorption efficiency. This property can be used to advantage for improving recovery. For example, if a desorption efficiency of 50% has been obtained by desorbing 100 mg of charcoal with 1/2 ml of carbon disulfide, by using 5 ml of solvent, an efficiency of 91% should be obtained. It also indicates that if the backup section containing one-half the amount of sorbent is desorbed in the same volume, a 5 to 15% positive error could be introduced.

temperature

The temperature effect on recovery can be significant. If high temperatures are encountered while sampling; decomposition, polymerization or other chemical reactions may occur on the activated surface of the sorbent. It is a common practice to cool the solvent before desorbing samples to reduce the heating effects. However, the equilibrium constant will change with temperature and the final desorption temperature may be critical. An efficiency change has been observed for MEK from 89.5% to 66.8% at 25°C and 0°C respectively.[18] The magnitude of the effect depends on the compound. Vinyl chloride shows no effect with desorption temperature in this range.[13]

humidity

High humidity during collection may produce low recoveries for compounds which are easily hydrolyzed. If a large amount of water is collected it may prevent good contact with a

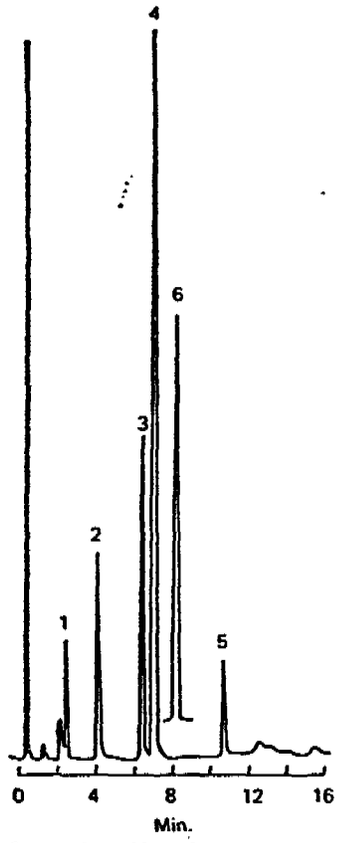

Figure 7 — Formation of interferences from methanol in a carbon disulfide and charcoal mixture.

TABLE III
Desorption Efficiency of Aromatic Compounds

Sorbent: Coconut Base Carbon 0.5 grams
Solvent: Carbon Disulfide 5 ml
Concentration: 0.2-0.3 mg/5 ml

	Desorption Efficiency	
	After 1 hr.	After 16 hrs.
Benzene	98	98
Toluene	98	98
Naphthalene	43	40
Biphenyl	55	53
Diphenyl Oxide	93	98
Diphenyl Methane	93	97
Para Methyl Biphenyl	84	

non-polar desorption solvent, or change the equilibrium if it dissolves in the desorption solvent. This effect is more pronounced with polar sorbents and can sometimes be counteracted by using longer desorption times and stronger (more polar) desorption solvents.

coadsorption

Collection of other compounds can also affect recovery. The chemistry of all the compounds collected must be considered and their relative effects tested in the laboratory.

desorption time

One-half to one hour with good agitation is usually sufficient desorption time for most systems. Once optimum desorption has taken place the system is generally stable; however, some exceptions have been observed.[19] Figure 6 shows the decrease in recovery for styrene monomer over a 16 hour period. This effect is more pronounced for lower concentrations. When this situation is observed, the extract should be removed from the sorbent if samples cannot be analyzed during the optimum desorption period. This type of decrease was not observed for the compounds listed in Table III.

It is also necessary to establish the stability of the solutions and reagents because of the possible catalytic effect of the activated sorbent surface. In some procedures using charcoal, 1% methanol is added to increase desorption efficiency, particularly for polar compounds. If the mixture is allowed to stand in contact with the charcoal longer than four hours a reaction takes place forming a number of peaks shown in Figure 7. Similar chromatograms were observed with Durapak® - Carbowax 400/Porasil F, 5% QFI or 5% OV 210 gas chromatographic column using a temperature program. Tentative identification by gas chromatography/mass spectrometry indicates dimethyl di-, tri-, and tetrasulfides, mercaptans and polyether - thioether compounds.[19] Ethanol gave one major peak (6), but no reaction peaks were observed with isopropanol.

storage

In most cases samples are not analyzed the same day they are taken, and some compounds may show low recoveries after a one or two week storage period. Refrigeration of the samples may

help or immediate desorption for later analysis can be used if the solutions are stable.

concentration

The phase equilibrium model predicts the desorption efficiency should not vary with concentration. For most methods developed for organics on charcoal, this concept is generally true (within ± 5%) for concentrations of interest in industrial hygiene samples. Some compounds have a tendency toward lower recoveries as illustrated by styrene monomer in Figure 6. As the concentration decreases a decrease in desorption efficiency is observed. Any factors which affect the recovery will usually have a greater percentage effect on the lower concentrations.

recovery prediction

Some extrapolations can be made from existing information but more data is necessary before accurate prediction can be made from physical and chemical properties. An example is shown in Table III which illustrates high attraction (low desorption efficiencies) for biphenyl and naphthalene and lesser attraction for similar compounds possibly because of bond angles or steric effects.[20]

experimental procedures

desorption efficiency

direct injection (static)

Desorption efficiency is usually determined by placing the sorbent from the front section of a collection tube in a small vial and injecting a known amount (a few μl) of the compound or solution of the compound directly into the sorbent at several points. The vial is capped and analyzed subsequently using the exact procedure to be used for the samples. Periodic analyses of this same solution over a longer time period (4-8 hours) can be used to optimize desorption time and determine a time limitation. If several preparations are made a week or more in advance, an estimate of the storage effects can also be made.

phase equilibrium

The phase equilibrium technique for determining desorption efficiency approaches the equilibrium from the other direction.[18] Known concentrations of the compound(s) to be studied are prepared in the desorption solvent and analyzed. An aliquot of this solution, equal to the volume used in desorbing samples, is cooled and the front section of sorbent from a sampling tube is added. The solution is analyzed periodically until a steady state is obtained.

preliminary bias and breakthrough studies

Although method bias and breakthrough will be determined more accurately during the validation procedure, early identification of excessive breakthrough or large differences between the desorption efficiency and total recovery of a simulated air sample may save considerable time. If the desorption efficiencies as determined by the direct injection are considerably lower than phase equilibrium values, interaction or reaction on the sorbent surface is indicated. If the total recovery from a simulated air collection is lower than the direct injection efficiency, even though no breakthrough has occurred, hydrolysis, oxidation, or other reaction may be indicated.

breakthrough and recovery

The factors which affect each of these have been discussed. The extent of the effects can be determined in the laboratory with simulated air sampling experiments. A number of systems for producing a known atmosphere have been suggested. These include air bags, permeation tubes, diluters, etc., and are discussed in detail in the literature.[22]

A device, adapted from the literature,[23] has been used with success for a wide range of liquids and solids.[24] Air, which is pulled through a saturated salt solution to create a known humidity, is swept through a U-tube, and carries the compound vapors into the collection tube.

Breakthrough for volatile compounds can be determined by monitoring the effluent by gas chromatography using a gas syringe or gas sampling valve. For compounds which cannot be monitored this way, tubes containing four sections of sorbent, each 1/2 the size of a field sampling tube can be used (the cross-section should be the same). Section no. 3 would represent the backup section and section no. 4 could be used to determine breakthrough. The different parameters are examined in subsequent runs by varying the concentration, humidity,

temperature of the collection tube, etc., and analyzing each section separately to determine sorption profiles. See Figure 5. After each run, the U-tube is rinsed with an appropriate solvent, which is analyzed to obtain a mass balance for each component.

A modification of this technique can be made for very low concentrations of high boiling materials such as pesticides.[25] An extra small glass wool plug is placed in the front end of the divided tube. A small amount of a dilute solution is injected into this plug at the start of a collection test. Analysis of the plug separately from the sections will give a mass balance.

criteria for a validated method

The factors which affect air sampling with solid sorbents can be quite complex. It is necessary to define some general criteria as a standard to evaluate acceptable methods and a guide to determine the data necessary to support the evaluation. The various steps in method development and validation can be divided into several sections as outlined in Table IV.

TABLE IV
Progressive Development and Validation Steps

Suggest procedure (little or no experimental work)
1. Chemical, physical, and toxicological properties listed.
2. Concentration range and required sensitivity estimated.
3. Sorbent-desorption system(s) extrapolated from similar compounds.
4. Analytical procedure suggested.
5. Possible interferences indicated.
Tentative procedure (limited experimental work)
1. Analytical procedure tested.
2. Desorption efficiency determined.
3. Optimized desorption time.
4. Preliminary breakthrough and bias study.
5. Preliminary field samples.
6. Effect of interferences, coadsorption and temperature (if indicated).
Validated method (systematic study)
1. Determination of breakthrough volume at concentrations of 2 times TLV and relative humidity of 85% or greater.
2. Five samples at each concentration, 0.1, 0.5, 1 and 2 times TLV for relative humidities less than 50% and greater than 85%. (40 samples).
3. Six samples at the TLV concentration (three collected at each humidity) and stored for at least 14 days.
4. Statistical evaluation of data.
5. Field validation by comparison to accepted method or by field spiking.
6. Collaborative studies with other laboratories.

TABLE V
Criteria for Successful Validation

1. Accuracy and Precision of Combined Analytical and Collection Procedures for concentration range of 1/10 TLV to 2 TLV — ±16% relative at the 95% confidence level.
2. Total Recovery efficiency of at least 75%.
3. Bias between Total Recovery and desorption efficiency less than ±10% relative.
4. Capable of taking 10-15 minute samples at ceiling and excursion levels.
5. Minimum sampling time one hour, preferred 4 to 8 hours for TWA.
6. Storage samples should compare within ±10% relative to initial samples after being stored for 14 days.
7. The flow rate of the sampling pump should be known with the accuracy of ±5%.

The amount of testing necessary depends on the extent of the sampling project. Methods for limited surveys, where the sampling conditions and concentrations are defined and relatively constant, can be validated for the specific situation. The minimum amount of data necessary will vary with the project, but a guideline such as the 10-10-10 principle,[26] or a recently suggested 7-7-7 principle for water effluent analysis, may be adapted. For a specific situation, this would involve seven determinations on controls (blanks and interferences), seven determinations on various concentrations for recovery data (spiked tubes) and seven determinations in a controlled or simulated air sampling situation to determine the precision of the procedure (specified humidity, temperature etc.). If additional sampling variables are subsequently introduced or if the procedure is proposed for general sampling, additional data should be obtained.

Specific guidelines, in Table V and discussed below, have been developed from the literature and study of a wide range of organic compounds in industrial areas. They are intended to indicate the degree of reliability which should be obtained from an acceptable method using diligent but practical application of developmental and sampling techniques. If a meth d fails to meet some of the criteria, it could still be used as long as its limitations are known and dealt with effectively.

It is important to point out that although a method is validated for a specific ppm v/v

concentration range (1/10 to 2 TLV) we are actually dealing with a specific weight of chemical. If much smaller volumes of air are taken for actual field samples, poor precision will reflect the low milligram amount collected even though the calculated ppm v/v concentration is within the range validated.

accuracy and precision

Accuracy, how close the observed value x is to the true value $\hat{x}$, can be expressed in terms of relative error.

$$\text{relative error} = \left(\frac{\hat{x} - x}{x}\right)100 \qquad (3)$$

The relative error can be separated into "determinate or systematic" errors and "indeterminate or random" errors. The systematic errors, which are unidirectional and are inherent in the method, are due to incomplete desorption, inefficient extractions, etc., and once determined can be expressed in terms of percent recovery, R. The deviations due to the random errors can be treated by an expression of precision.

After the series of recovery experiments the data are treated by calculating the standard deviation σ and applying it in equations (4) (5) and (6).

The relative precision for a single determination, RPs, at the statistical confidence level of 95%, is given by equation (4), with a determined average percent recovery, Rn, for n number of determinations.

$$RPs = \pm \frac{2\sigma}{Rn} \times 100 \qquad (4)$$

The relative precision for the determination of average percent recovery, RPn, is

$$RPn = \frac{RPs}{\sqrt{n}} \qquad (5)$$

If the validation data has been obtained using a mass balance generation technique such as direct injection or U-tube, the contribution of pump precision, RPp must be considered. The total relative precision, RP_T, is then given by equation (6).

$$RP_T = \sqrt{(RPs)^2 + (RPn)^2 + (RPp)^2} \qquad (6)$$

The true concentration, C, for any experimentally determined concentration Z, is given by equation (7) when Rn and RP_T are given as a percent:

$$C = \left(\frac{Z}{Rn}\right)\left(100 \pm RP_T\right) \qquad (7)$$

Statistical treatment of data obtained as suggested in Table IV will establish an overall precision of the total recovery and help identify any bias. Data should be obtained for the lower concentration of 1/10 TLV since many areas contain mixtures of several compounds. If methods are validated for concentrations only down to 1/2 TLV, it would be difficult to support data for mixtures of more than two compounds as indicated by the ACGIH additive rule.[28]

The suggested precision guidelines of ±16% were developed from several groups of information. Data has been obtained in our laboratories for the collection and analysis of over 50 compounds for sampling periods of 4 to 8 hours. The average relative precision was ±6.5% with a range of ±3% to ±10% at the 95% confidence level (not including sampling pump precision).

Out of the 98 NIOSH methods published for solid sorbent-gas chromatographic techniques,[28] 87 fall within ±16% relative precision level with less than ±12.9% relative precision at the 95% confidence level. In another study,[29] where fifteen investigators sampled seven different compounds, each over a range of 5% to 2 times the TLV (a total of 300 samples by each person), the relative error in the range of 60% TLV to 2 times the TLV was ±12.7%. At a concentration of 5% of the TLV, the relative error was double or approximately ±25%. All the samples were taken for 10 minutes.

bias, desorption efficiency and total recovery

By treating the various groups of data separately, a bias may be detected when the recovery varies as a function of a parameter such as concentration, humidity, storage, flow rate etc., even though no breakthrough has occurred. When such a bias, (the difference between the desorption efficiency and total recovery,) is observed to be greater than ±10%, it should be plotted as a function of the variable and a correction for it included in the method. When bias is observed for more than one parameter the collection and recovery procedures should be reconsidered.

sampling time

A one hour sampling period may be sufficient to determine a time weighted average (TWA). A more accurate value can be obtained with a longer sample especially in areas where the atmosphere varies greatly or when personnel spend a large part of their time in a number of different areas. In most cases the procedures used for long term samples will work for short term samples when determining ceiling and excursion values. If it is necessary to increase the flow rate to obtain the required sensitivity, additional breakthrough data will be necessary.

sampling pump

One of the largest errors which can be introduced into a validated method is inaccurate sample volume measurement. The flow rate of a pump can be measured within ±5%; however, the flow rate may change as the batteries are depleted. Digitized pumps will measure an accurate volume but may introduce a bias since the strokes per minute may decrease. This effect becomes more important with long sampling periods. A periodic check of the performance curve of each battery operated pump should be made. Sampling equipment is being continually improved, and good accuracy can be obtained with careful calibration and use.

field testing

Although many of the collection and recovery parameters can be tested in the laboratory, it is not often possible or feasible to simulate actual field sampling conditions. Judicious field testing during method development and after a successful validation will either uncover unpredictable circumstances or increase confidence.

One technique used in field testing is on-site comparison to an established (but possibly inconvenient) alternate method. The alternate procedure may be a time averaging technique such as a portable infrared, or use of periodic short term or instantaneous grab samples.

Field spiking is also a useful technique where a duplicate sampling system is set up in an on-site area. One of the collection tubes is then spiked with an appropriate amount of the test compound. Identical treatment and analysis of the duplicate tubes will indicate the unknown concentration in the area as well as the recovery factor from the spiked tube by difference. Direct injection spiking can be used in field samples if no bias has been observed between this technique and dynamic spiking techniques.

Several unused tubes, to serve as blanks, and several spiked tubes containing appropriate amounts of the expected compounds should be included with the samples as a check on storage, transportation factors and analytical procedures. Widely varying recoveries will signal difficulties and the necessity to reevaluate the data but should not be used for correcting the results.

communications

The development, sampling and analytical sections of a survey are strongly interdependent and it is important that the specialists working on each section have a basic understanding of the total effort. Good communications before, during, and after are essential factors in a successful validation and sampling project.

references

1. Linch, B. E.: Quality Control for Sampling and Laboratory Analysis. *The Industrial Environment - Its evaluation and Control.* NIOSH, Government Printing, Washington, D.C.
2. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
3. MSA Research Corporation: Package Sorption Device System Study. EPA Contract EHSD 71-2, National Technical Information Service, PB-221 138.
4. Jonas, L. A. and J. A. Rehrmann: Predictive Equations in Gas Adsorption Kinetics. *Carbon 11*:59 (1973).
5. Jonas, L. A. and J. A. Rehrmann: The Rate of Gas Adsorption by Activated Carbon. *Carbon 12*:95 (1974).
6. Nelson, G. O. and C. A. Harder: Respirator Cartridge Efficiency Studies: VI; Effect of Concentration. *Am. Ind. Hyg. Assoc. J. 37*:205 (1976).
7. Fraust, C. L. and F. R. Hermann: The Adsorption of Aliphatic Acetate Vapors onto Activated Carbon. *Am. Ind. Hyg. Assoc. J. 30*:494 (1969).
8. Saltzman, B. E.: Basic Theory of Gas Indicator Tube Calibration. *Am. Ind. Hyg. Assoc. J. 23*:112 (1962).
9. Wood, G. O. and R. G. Anders n: Personal Sampling for Vapors of Aniline Compounds. *Am. Ind. Hyg. Assoc. J. 36*:538 (1975).
10. Novak, J., V. Vasak and J. Janak: Chromatographic Method for the Concentration of Trace Impurities in the Atmosphere and other gases. *Anal. Chem. 35*:735 (1963).

11. Pesek, J. J., and J. E. Daniels: Investigation of the Retention Mechanism of Chemically Bonded Stationary Phases in Gas Chromatography. *J. Chrom. Sci. 14*:288 (1976).
12. Severs, L. W. and L. K. Skory: Personnel Sampling and Analysis of Vinyl Chloride. *Am. Ind. Hyg. Assoc. J. 36*:669 (1975).
13. Hill, Jr., R. H., C. S. McCammon, A. T. Saalwaechter, A. W. Teass and W. J. Woodfin: Gas-Chromatographic Determination of Vinyl Chloride in Air. Samples Collected on Charcoal. *Anal. Chem. 48*:1395 (1976).
14. Teass, A. W., C. S. McCammon, C. P. Roper and A. T. Saalwaechter: Sampling Organic Vapors Using Activated Charcoal. *2nd NIOSH Solid Sorbent Roundtable, Cincinnati, Ohio, December 1973.* HEW Publication No. (NIOSH) 76-193 (1976).
15. Ballou, E. V.: An Overview of the Use of Solid Sorbents for Air Analysis. *2nd NIOSH Solid Sorbent Roundtable, Cincinnati, Ohio, December 1973.* HEW Publication No(NIOSH) 76-193 (1976).
16. Fraust, C. L. and F. R. Hermann: Charcoal Sampling Tubes For Organic Vapor Analysis By Gas Chromatography. *Am. Ind. Hyg. Assoc. J., 27*:68 (1966).
17. Nelson, G. O., A. N. Correia and C. A. Harder: Respirator Cartridge Efficiency Studies: VII; Effect of Relative Humidity and Temperature. *Am. Ind. Hyg. Assoc. J. 37*:280 (1976).
18. Dommer, R. A. and R. G. Melcher: Phase Equilibrium Method for Determination of Desorption Efficiencies. *Am. Ind. Hyg. Assoc. J. 39*:240 (1978).
19. Irwin, M. M. and W. Kracht: Unpublished Data, The Dow Chemical Company, Midland, Michigan.
20. Melcher, R. G.: Unpublished Data, The Dow Chemical Company, Midland, Michigan.
21. Kerr, M. L.: Unpublished Data, The Dow Chemical Company, Midland Michigan.
22. Saltzman, B. E.: Preparation of Known Concentrations of Air Contaminants. *The Industrial Environment-Its Evaluation and Control.* NIOSH, Government Printing, Washington, D.C.
23. Whitman, N. E. and A. E. Johnston: Sampling and Analysis of Aromatic Hydrocarbon Vapors in Air: A Gas-Liquid Chromatographic Method. *Am. Ind. Hyg. Assoc. J. 25*:464 (1964).
24. Severs, L. W., R. G. Melcher and M. J. Kocsis: Dynamic U-Tube System for Solid Adsorbent Air Sampling Method Development. *Am. Ind. Hyg. Assoc. J.* In Press.
25. Melcher, R. G., L. W. Severs, M. J. Kocsis and W. L. Garner: Specialized Solid Sorbents for Sampling Organic Compound of High and Low Volatility in Air. Presented at *172nd ACS National Meeting, San Francisco* (1976).
26. Kagel, R. O.: Analytical Problems in Effluent Analysis, Presented at Manufacturing Chemist Association *Symposium on the Approaching Toxic Era* (1976).
27. American Conference of Governmental Industrial Hygienists: TLVs, *Threshold Limit Values for Chemical Substances in Workroom Air Adopted by ACGIH for 1976.*
28. NIOSH Analytical Methods for Set A-J Standards Completion Program. National Technical Information Service, Springfield, Virginia.
29. NIOSH Contract HSM-99-72-98, Scott Research Laboratories, Inc.: *Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Compounds* HEW Publication (NIOSH) 76-173 (1976).

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Comments now wanted . . . revision on occupational exposure to ozone standard now in progress

The ASTM task force on Occupational Exposure to Ozone is revising the ASTM standard practice (E-591) for Safety and Health Requirements Relating to Occupational Exposure to Ozone. The task force is under the aegis of Committee E-34 on Occupational Health and Safety Aspects of Materials, Physical and Biological Agents.

These voluntary consensus guidelines establish recommendations in industrial hygiene, industrial medicine, safety engineering, engineering controls and monitoring, with appropriate toxicological and epidemiological rationales, relating to occupational exposure to ozone. The current revision to the standard incorporates significant changes in the appendix (rationale) detailing Biological Effects of Exposure to Ozone on Humans.

Due to the extensive nature of this standards development activity all areas of expertise are encouraged to participate. Upon request, therefore, a copy of the standard will be provided for comment. The current revision will be discussed at the upcoming meeting of E-34, May 21-23, 1978, Radisson Muehlebach, Kansas City, Missouri.

For further information and/or a copy of the working draft standard, contact the staff manager, Donald A. Tobias, ASTM, 1916 Race St., Phila., PA 19103 (215) 299-5546.