PATTY'S INDUSTRIAL HYGIENE

Sixth Edition

Volume 1
HAZARD RECOGNITION

11

SAMPLING AND ANALYSIS OF GASES AND VAPORS*

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1 INTRODUCTION

Only a few exposure limits for chemicals are couched in terms of a maximum allowable concentration for any given instant because most chemical illnesses occur as a response to a cumulative dose rather than a response to peak exposures. Even in the exceptional cases, some form of time-integrated measurement is usually performed because of the extraordinary resources that would be required to monitor every worker for every moment of their shift. The time period for integration of measurement for toxins with a chronic effect is usually a full work shift, which has traditionally been considered as 8 h (480 min). It was assumed that 5 days of work with exposure at the chronic exposure level were punctuated by a weekend without exposures, and the consequent nightly and weekend recovery periods had been incorporated into pharmacologically based models of metabolism. Today, variations in this work pattern are commonly encountered, and various alternative models have been put forward to account for extended exposures and shorter periods without exposure. Toxins with more acute effects are evaluated on the basis of a shorter exposure period, traditionally 15 min, and the frequency of these short-term exposures and the amount of time between them are also controlled. The standard method for assessing exposures is

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* Disclaimer: The findings and conclusions in this chapter are those of the author and do not necessarily epresent the views of the National Institute for Occupational Safety and Health. Mention of sampling devices does not constitute an endorsement and does not imply that other devices are fit for the same purpose.

Patty's Industrial Hygiene, Sixth Edition, Edited by Vernon E. Rose and Barbara Cohrssen

to measure the toxins in a known volume of air averaged over the appropriate period, 8 h or 15 min, or some other appropriate time. Dividing the mass of toxin collected on a sampling device by the volume of air sampled gives a concentration that can be compared to values set as guidelines or regulations for safe working. For extremely acute responses, it may be necessary to establish a ceiling level above which exposures should not occur, and these are monitored by systems with direct readout and often including alarms.

Occupational or industrial hygiene sampling is performed for several reasons: to identify and quantify the contaminants present in the work environment, to identify emission sources, and to evaluate the effectiveness of engineering controls installed to minimize workers' exposures, but mostly to determine exposures of workers in response to complaints or outbreaks of disease, or to assess compliance with respect to various occupational exposure standards, or to determine the exposures of a worker or group of workers over time, in order to get baseline data to compare with disease prevalence. The reasons for sampling dictate to some extent the sampling strategy that should be used. Area sampling can be conducted in a strategic pattern to document the environmental characteristics of the workplace. Sampling can be conducted around control measures such as local exhausts to determine how well they are operating. Mobile sampling can be used to determine emission sources (leaks). Personal breathing zone samples are typically obtained to document actual worker exposures. This requires that the inlet of the sampling device be close to the nose and mouth of the worker, usually defined as being within a hemisphere of about 30 cm radius extending from the midline of the nose and mouth. The most common location for personal sampling devices is therefore the lapel of the workers' clothing. In the absence of a lapel, straps of a back-support belt or a headset-type sampling media holder have been used to locate the sampling devices appropriately. The substances being monitored determine the type of sampling to be used; limitations of the sampling device may dictate sampling time and sampling rate. Analytical laboratory requirements may require that a minimum mass of the substance be collected. In short, consideration must be given to a number of variables when contemplating a sampling campaign.

Many sampling methods available to the industrial hygienist have become standardized and require relatively little experience to apply. In some countries, sampling has become the role of an industrial or occupational hygiene technician. On the other hand, some tests call for an understanding of chemistry and may require a more qualified specialist. At one time, this was considered so much the case that the American Board of Industrial Hygiene recognized a unique certification in the Chemical Aspects of Industrial Hygiene. However, although there are still some certified individuals the examination for this specialty has not been offered for many years. In lieu of specialist training, field personnel are strongly advised to consult with the chemists in their analytical laboratory before embarking on a sampling exercise in the workplace. Since the vast majority of samples will be analyzed by chemical methods, the laboratory will have valuable insight into the possibility of interfering chemicals or environmental conditions that might compromise the accuracy of sample results. Typically, this conversation can be initiated at the time of ordering the sampling media, since it is not common for industrial hygienists to order media directly from the manufacturer but from the laboratory to which they expect to submit he samples. The benefits are mutual; the laboratory is assured of the analytical work nd the industrial hygienist is assured of using the correct sampling media. The ygienist is not required to purchase media that may have a limited shelf life, and also s assured that the laboratory has the capability to perform the analysis.

The final decision regarding the method of sampling and analysis depends on the roblem at hand rather than mere rote application of a standard method. Methods with high degree of accuracy are given preference because of the legal significance f occupational health standards, for example, as promulgated in the United States nder the authority of the Occupational Safety and Health Act of 1970. With this Act xposures to a large number of chemicals in the workplace became regulated and methods for assessing exposure were urgently required. The U.S. National Institute for Occupational Safety and Health (NIOSH) under the Standards Completion Program was responsible for developing many methods that are used today (1). In addition, the U.S. Occupational Safety and Health Administration (OSHA) also develops analytical methods that are used when sampling and analyzing the many contaminants in the workplaces for which it has regulations (2). In Europe, examples of agencies developing methods include the U.K. Health and Safety Laboratory (HSL) (3), the French Institut National de Recherche et de Sécurité (INRS) (4), and the German Research Foundation (Deutsche Forschungsgemeinschaft) (5) or the Berufsgenossenschaftliches Institut für Arbeitsschutz (BGIA) (6). European methods are generally expected to meet performance requirements established by European Standards. Methods may also have been established by similar agencies in other countries. A valuable compendium of method references, together with a guide to their validation status is available on-line (7).

A substance is considered to be a gas if at room temperature and ambient atmospheric pressure its normal physical state is gaseous. A vapor is the gaseous state of a substance that is in equilibrium with the liquid or solid state of the substance at ambient temperature and atmospheric pressure. This equilibrium results from the vapor pressure of the substance causing volatilization or sublimation into the atmosphere. The sampling techniques discussed in this section are applicable to a substance in gaseous form regardless of whether it is technically a gas or a vapor. Gases and vapor concentrations are often discussed in terms of the ratio of the pressure or volume of the gas or vapor to the total pressure or volume of the atmosphere (volume ratio is usually expressed in units of parts per million, ppm, or parts per billion, ppb). Alternatively, concentrations can be presented in terms of the mass of contaminant per unit volume of air (e.g., mg/m^3). For many chemicals, the toxic effects are related to the mass dose of the chemical, which can be quickly determined from the concentration in mass per unit volume, when the volume of air breathed by the worker is known, and also the amount of chemical absorbed from the air during breathing (normally assumed to be 100%). Given that a worker will acclimatize the physiology of respiration to different air pressures, breathing rates for different types of work are relatively constant at different altitudes, so that the same concentration expressed in mass per unit volume will lead to the same dose, no matter the altitude, assuming the same type of work. This is not the case for concentrations expressed in volume ratio terms, as the same volume ratio will contain a different mass of chemical at different pressures (and also temperatures). Thus, when concentrations are calculated in volume ratios, they must be adjusted for a specific pressure and temperature in order to be compared with regulatory or guideline concentrations expressed the same way. The specific temperature and pressure used in the United States are 760 mmHg and 25°C, respectively, and this is referred to as normal temperature and pressure (NTP). However, 20°C may be used elsewhere. Regulatory concentrations from OSHA and threshold limit values (TLVs®) issued by the American Conference of Governmental Industrial Hygienists (8) are given in terms of "ppm at NTP." When OSHA exposure standards are listed as ppm, the mg/m^3 value is calculated from the ppm value and it is approximate.

The work environment often houses many chemicals, which may be in use simultaneously, for example, in solvent mixtures, or sequentially. In many cases, these chemicals may have additive effects, especially where they affect the same target organ. Limit values with similar basis of time intervals are easily combined for different chemicals in an additive formula. Thus, for concentrations $C_1, C_2, \ldots, C_n$ of chemicals with corresponding limit values $T_1, T_2, \ldots, T_n$, the sum of

$$\frac{C_1}{T_1} + \frac{C_2}{T_2} + \cdots + \frac{C_n}{T_n}$$

should not exceed unity. It is also possible in some cases to combine limit values with different time bases, but the situation is more complex. Guidance can be found in the *ACGIH Threshold Limit Values* handbook (8). The additive model also applies to sequential exposures of different substances that occur during the same shift, where the situation is generally handled as if they were the same substance. In the absence of information to the contrary, different substances should be considered as additive where the health effect and target organ or system are the same. Exceptions to this rule include substances that have an inhibitory or synergistic effect, and care should be exercised in dealing with mixtures that include suspect or known human carcinogens.

The following are not subjects of this chapter:

a. Strategies for sampling in the workplace and their statistical basis (Chapters 13 and 18);
b. Direct reading instruments for monitoring gases and vapors;
c. Sampling techniques for particulate contaminants (Chapter 8);
d. Biological monitoring as it relates to industrial hygiene sampling (Chapter 13),
e. Sampling of surfaces (Chapter 13) or assessment of exposure to skin (Chapter 3).

The objective of this chapter is to describe the basis for sampling and analytical methods for gases and vapors rather than the methods themselves. Relatively complete discussions of detailed methods of analysis for specific contaminants are presented elsewhere in this series.

2 GENERAL CONSIDERATIONS

Chemical and physical stresses can be evaluated in various ways. One form of evaluation is qualitative, that is, using the industrial hygienist's powers of observation without taking any actual measurements. This kind of inspection and evaluation of a work situation is commonly called the "Walk Through" and it can provide valuable information, particularly when performed by an experienced industrial hygienist. Another form of evaluation is quantitative, involving collection and analysis of samples representative of actual workers' exposures. Generally, this kind of evaluation is more desirable when the purpose of the sampling is to determine compliance with occupational health exposure standards.

2.1 Qualitative Survey

An experienced professional industrial hygienist often can estimate, quite accurately and in some detail, the magnitude of chemical and physical stresses without requiring any actual measurements. In fact, most professionals use this qualitative evaluation every time they make a survey, and it is an important part of their work prior to actual sample collection and laboratory analysis. Qualitative evaluation can be applied by anyone familiar with an operation, from the worker to the professional investigator, to ascertain some of the potential problems associated with work activities.

The first step in evaluating the occupational environment is to become as familiar as possible with particular operations. The person evaluating the operation should be aware of the types of industrial process and the chemical raw materials, by-products, and contaminants encountered. The evaluator should also know what protective measures are provided, how engineering controls are being used, and how workers are exposed to contaminants generated by specific job activities. The value of open and frank dialogue with personnel actually performing tasks in the workplace should not be underestimated.

It is important that responsible industrial hygienists establish and maintain lists of the chemical and physical agents encountered in their particular areas of jurisdiction. Chemical inventories are usually a legal obligation on the part of the employer. The number of chemical and physical agents capable of producing occupational illnesses continues to increase. New products that require the use of new raw materials or new combinations of familiar substances are continually being introduced. This is particularly true in the chemical industries where new chemical products and operations for their processing are being developed. The composition of the products and by-products and as many of associated contaminants as possible should be known. This means that the industrial hygienist must obtain complete information on the composition of various commercial products. In most instances, the desired information can be obtained from descriptive material provided by the suppliers in the form of a Material Safety Data Sheet. Similarly, labels on containers of the material should be read carefully. Although there are explicit requirements under hazard communication and right-to-know regulations, labels still do not always give complete information, and further investigation into the composition of the materials is necessary. After the inventory is obtained, it is necessary to determine the toxicity and other hazardous properties of the chemicals. Information of this type can be found in several excellent reference texts on toxicology and industrial hygiene, or from the product manufacturer.

During a qualitative walk-through evaluation, many potentially hazardous operations can be detected visually. Operations that produce large amounts of fumes can be observed, and the sense of smell can be used to detect the presence of many vapors and gases. Although it is often possible to determine the presence or absence of potentially hazardous physical agents at the time of the qualitative evaluation, rarely can the potential hazard be evaluated without the aid of a more rigorous model with inputs designed to lead to a semiquantitative prediction of the exposure concentration (see Chapter 17 for further details). Inputs such as the amount of chemical in use, and the likelihood that they may evaporate (process operating temperature and vapor pressure or boiling point), can be used to make these estimates. Sophisticated models have been developed, such as the Estimation and Assessment of Substance Exposure (EASE), or the Multi-Chamber Concentration and Exposure Model (MCCEM), or the Bayesian Exposure Assessment Toolkit (BEAT). Exposure assessments from models can be combined with assessments of toxicity to determine levels of risk and can drive control recommendations using a procedure known as control banding (CB) (9). Examples of CB tools include COSHH Essentials, Stoffenmanager, and the ILO Toolkit. Such risk assessment and management models are becoming very popular as companies use them as an aid to compliance with the Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) regulations, which came into force in the European Union on June 1, 2007. However, such assessments do not absolve employers of responsibility for compliance with occupational health and safety regulations, including compliance with prescribed exposure limit values. Noncompliance with occupational exposure limits may be regarded as a criminal offense and subject to severe penalty. For this reason, accurate assessment is required using an analytical method of proven capability.

2.2 Quantitative Survey

Although the information obtained during a qualitative evaluation of a facility is important and always useful, only by measurement can the hygienist document the actual level of chemical or physical agents associated with a given operation. The strategy used for any given air sampling program depends to a great extent on the purpose of the study. Three general locations are used for collection of air samples: at a specific operation, in the general workroom air, and in a worker's breathing zone. The choice of sampling location is dictated by the type of information desired, and a combination of the three types of sampling may be necessary. Evaluation of a worker's daily time-weighted average exposure is best accomplished, when analytical methods permit, by allowing the person to work a full shift with a personal sampler attached in their "breathing zone." The concept of full-shift integrated personal sampling is much preferred to that of short-term or general area sampling, especially if the results are to be compared with exposure standards based on time-weighted average concentrations. When methods that permit full-shift integrated sampling are not applicable, time-weighted average exposures can be calculated from consecutive short-term exposures, weighted according to the time spent in various areas or on various tasks for which the exposures can be reliably estimated. Most exposure standards are written for an employee's personal exposure.

When sampling is done for the purpose of comparing results with airborne contaminants whose toxicological properties warrant short-term and ceiling limit values, it is necessary to use short-term or grab sampling techniques to define peak concentrations and estimate peak excursion durations. For purposes of further comparison, 8 h time-weighted average exposures can be calculated using the time-weighted sum of values obtained by consecutive short-term sampling.

The airborne concentrations of chemicals or exposure to physical agents can be quite different for each shift. It usually is desirable to obtain samples during both summer and winter months, particularly in plants located in areas where large temperature variations occur during different seasons of the year. For one thing, there generally is more natural ventilation provided to dilute airborne contaminants during the summer months than during the winter months.

2.3 Sampling Instrumentation

In general, the choice of instrumentation when sampling for a particular substance depends on a number of factors. While direct reading instruments are sometimes technologically advanced, they have significant drawbacks when used to determine full-shift time-weighted average concentrations. In addition to potential limitations on specificity and sensitivity, direct reading instruments are generally quite expensive and may require the constant presence of an operator. In addition, quality control for sample results is difficult to maintain. However, for some gases and vapors, for example, chlorine, hydrogen sulfide, and carbon monoxide, where acute hazards are likely to occur and also likely to have severe consequences, small and sophisticated sensors have been developed and these make very valuable contributions to worker safety, and, if they have data-logging capabilities, they can also be used to determine compliance with exposure standards. In addition, some simple, field identification kits are available for on-site end-shift analysis, allowing more rapid response to unhygienic housekeeping conditions.

For other chemicals, with less acute effects, air samples are generally taken and analyzed off-site in a laboratory (10). The sampling instruments used for this purpose are those that collect a fixed volume of air (whole air) and those that collect and concentrate the contaminants of interest from a fixed volume of air. The former type were used in the early days of industrial hygiene and are now enjoying a renaissance because of better equipment and some inherent advantages.

The most prevalent methods for gas and vapor sampling involve passage of a known volume of air either through an absorbing solution (bubbler) or through an adsorbing medium (tube) to remove the contaminants of interest from the sample air stream, or by allowing the contaminant molecules of interest to diffuse from the ambient air onto an absorbing or adsorbing medium across a fixed pathway. The former technique is known as "active," or pumped, sampling and the latter is known as "passive," or diffusive, sampling. Both techniques sample the atmosphere over an extended period of time, thus integrating the sample. The contaminant that is removed from the air stream becomes concentrated in or on the collection medium; therefore, it is important to establish a sampling period long enough to permit collection of a quantity of contaminant sufficient for subsequent analysis but not so long that the capacity of the collection medium is exceeded.

Sampling Pumps. Active integrated air sampling requires a known and controllable source of suction to move the air through the sampling medium. A vacuum line with sufficient pressure and a flow-restricting device, if available, may be satisfactory. However, the most practical and portable source for prolonged periods of sampling is a pump powered by batteries. These pumps come in various sizes and types and must be selected for the sampling devices with which they will be used. Because the flow rates employed for gas and vapor sampling are generally low (less than 1 L/min, and often as low as 10–20 mL/min but not so low that molecular diffusion into the sampler can occur), and because the pressure drop through the sampling medium is not large, the pumps need not be very big or powerful and can be run by small dry-cell batteries. A screw adjustment and an external calibration device is traditionally used to set and measure the flow rate, but more modern pumps have software control and internal flow sensors so that the desired flow rate can be "programmed in" by the user. Compensation for cyclic variation in flow is not as necessary for sampling gases and vapors as it is for sampling aerosols, where size selection requires a specific flow rate with minimal fluctuation. Therefore, even simple piston pumps can be used. However, all pumps must be capable of running unattended for the required time period, periodic checks on the airflow should be made when possible, and the pump must be calibrated before and after sampling. Air sampling pumps should also not be subject to or be sources of radiofrequency interference. If the pumps are to be used in atmospheres that are flammable they must be designed and certified as intrinsically safe for use in such atmospheres.

Sampling Rate Measurement. The flow rate through the active sampler must be known accurately. Calibration is required at the beginning and at the end of the sampling period and the measured flow rates should be within 5% of each other. External calibration is required for pumps with an internal flow sensor because the flow sensor is not a primary calibrator. External calibrators must be checked annually to maintain traceability to national or international standards, and this includes electronic calibrators. Calibration must take place with the type of sampling media to be used in-line. Common mistakes include calibration without the sampling media or calibration by placing the calibrator between the sampling media and the pump instead of before the sampling media. The sampling period must be timed carefully with a stopwatch or with the timing device incorporated into the most recent models of pumps, where it has been shown to be accurate. Sampling flow rates can and should be checked periodically in the field with a rotometer to ensure continued operation of the pump. Some pumps are equipped with flow-sensing devices that shut down the pump if flow falls below a certain level while also recording the time at which this occurs so that the sample to that point may still be useful. Where a sampling exercise requires a hygienist to make many measurements on the same day, it is easy to see how the workload of calibration may make passive samplers that do not require any calibration a more attractive option.

2.4 Duration of Sampling and Sampling Rate

In most cases, the industrial hygienist can choose between sampling for a few minutes and sampling for an entire work shift, and this allows sampling to be either task-based or full shift. However, each analytical laboratory uses procedures that require some minimum amount of material for reliable analysis. This should be known in advance by the industrial hygienist, and the minimum sampling period should be selected accordingly. Should a specific sampling period be required, but if this would not allow collection of sufficient contaminant for analysis, then the sampling rate sampled can generally be increased to compensate for the short time period, although there is a maximum (and a minimum) sample volume constrained by the method. Whole-air samples are limited by the maximum volume of the sampling container, while sampling methods that extract contaminants from a pumped stream of air where sample volume can be increased by increasing the flow rate are constrained by the pressure drop across the system, which rises with flow rate. In cases of chemical derivatization with reagent-coated sampling media, the reaction rate of contaminants with the media may require a low flow rate to allow adequate reaction time.

3 QUANTITATIVE SAMPLING

Gases and vapors form true solutions in the atmosphere and thus require either sampling of the total atmosphere using a whole-air collector or the use of a scrubbing mechanism such as a charcoal tube to separate the gas or vapor molecules from the surrounding air molecules in a known volume of air. The scrubbing mechanism can be absorption by solution in a liquid, adsorption on a solid adsorbent, or by reaction with another chemical, either in solution or on a coated solid. This scrubbing procedure was introduced because contaminant molecules can be extracted and concentrated from a relatively large volume of air allowing good analytical sensitivity from a small sampler. When procedures for scrubbing contaminant molecules from air were first introduced, a pump was used to pull air through the scrubbing apparatus. These procedures became popular for personal exposure measurement when small, lightweight pumps were developed that could be carried by the worker with ease. Even more acceptable to the worker are scrubbers that allow contaminant molecules to diffuse to the scrubbing apparatus without need of a pump. Other methods of sample collection by scrubbing, especially those relying on a solution in a bubbler, may be less efficient and less convenient to use for sampling. Extraordinary advances in analytical sensitivity in the laboratory now allow relatively small volumes of captured air to be analyzed, so that whole-air collection procedures are becoming more useful. These methods now have acceptable recoveries for the contaminant of interest. This is because of the development of surface passivation techniques for the container involving the deposition of a thin coating of fused silica on surfaces that might come in contact with the sample.

3.1 Active Sampling

3.1.1 Whole-Air Sampling (11) The most basic method for collecting whole-air samples involves the use of a container, such as a bottle, a flask, or a bag, to obtain a volume of the contaminant-in-air mixture. The temperature and pressure at the sampling site should be recorded so that any necessary adjustments to the analytical results can be made. If the container is filled quickly, this is called grab sampling and the sample is representative of atmospheric conditions at the sampling site at a given point in time. Glass bottles are sometimes used as containers, but passivated stainless steel flasks are much more robust. The flasks are evacuated, and grab sampling is achieved simply by opening the container to the atmosphere. Alternatively, the flasks can be connected to mechanisms that allow air to enter into the container at a controlled rate over a period of time. The combination of different size containers and different flow controllers allows selection of different time periods and sample sizes. Typically, the samples are around 0.25–1 L, which is sufficient for most analytical purposes. This size of flask can be easily worn by the worker. A thin PTFE (polytetrafluoroethylene) tube with one end open and attached to the worker in the breathing zone can be used to lead air to the flask that is located on a holster around the waist. It must be confirmed that there is no sample loss on the PTFE tube. At the laboratory, the sample can be removed from the flask either by pumping it out or by adding an inert gas to overpressure the container. The air from the flask is generally led through a small sorbent bed at subzero temperature that traps the chemicals of interest for subsequent analysis. The flask is then cleaned, usually with steam under pressure, evacuated and returned to use. The advantage of this technique over the more common trapping of chemicals in the field is that most chemicals are stable in the flask (since gas-phase reactions are slower than reactions in liquids or on surfaces) and all chemicals in the sampled air are collected.

Polymer bags can also be used as whole-air sample containers. These are cheaper than the evacuated flasks. They are usually made of an inert polymer, with polyvinyl fluoride (Tedlar®), or PTFE as the most popular. They come in a range of sizes from less than 1 L to more than 10 L capacity. They include a closeable port for filling and evacuation, and often a septum for removing sample or for adding gases and liquids (these bags are very commonly used to prepare calibration gas standards for direct reading instruments). The air sample can be fed into the bag through a pump connected to the port at a controlled rate or drawn in by a vacuum applied to the exterior of the bag, also at a controlled rate. The former technique can lead to bias through contamination of the sample or loss from the sample during passage through the pump. Sampling pumps with inert parts are available to minimize such bias. The latter technique for filling involves pumping air out of a rigid box containing the bag, the bag being open to the atmosphere and filled as air is removed from the box. This assembly is, however, too cumbersome for personal sampling. In addition to these methods for time-weighted sampling, grab samples can be taken by placing the bag inside a large syringe and pulling back on the plunger, again to evacuate the region around the bag so that air rushes in to the opening of the bag to fill it. In general, these bags are not often used for air samples because losses of chemicals occur over time through diffusion into the polymer or absorption on the fittings. This sampling technique requires that analysis take place as soon as possible after sampling. In addition, the material of the polymer may add contamination to the sample. Polymer bags are rarely used for personal sampling because it is not easy to find a good location on the worker to place the expanding bag.

3.1.2 Absorber Sampling While several types of absorbers are available for collecting gases and vapors, the spill-proof midget fritted bubbler is the only practical device in use for personal sampling, and even the use of this device has become quite rare in routine exposure sampling, as the trend is to replace liquid media with solid collection media for ease of handling and safety. Nevertheless, there are still a number of methods requiring bubblers in the literature. The frits on the bubblers are designed to maximize the bubble population and thus the surface area of contact between the air and the liquid. For some chemicals, such as isocyanates, which can exist in both vapor and solid phase, it is necessary to use an impinger so that particles are not trapped in the frit. However, impingers do not have the same collection efficiency as bubblers, and, in the case of isocyanates, a chemically coated filter is placed behind the impinger to catch fine particles or vapors. Bubblers are suitable for gases and vapors that are readily soluble in the absorbing liquid, but Henry's law of solution predicts a collection efficiency that will be reduced over time as the solution becomes more concentrated. One way to avoid this saturation is to provide a chemical in solution that reacts with the chemical of interest. This chemical may also be selected to stabilize a reactive chemical of interest or to make it more amenable to analysis (derivatization). Flow rates between 0.5 and 1.0 L/min are used commonly, but the pressure drop across a fritted bubbler is higher than that across an impinger and this may require a lower flow rate to be used. Excessive frothing can cause liquid to be forced into the tubing connecting the absorber to the pump, and so a trap tube is typically placed in line. In any case, evaporation of the liquid will take place over time, which can limit the sampling time to less than 1 h. Shipping restrictions need to be followed for liquid sampling media that are toxic or corrosive.

3.1.3 Adsorber Sampling (12, 13) This is the method of choice for collecting gases and vapors, and the vast majority of air sampling methods employ a solid adsorbent. Solid adsorbents require less manipulative care than do liquid absorbents and they are generally highly efficient at collection with only a small quantity of adsorbent (typically 100–200 mg), so that the sampling device is small and unobtrusive. The most powerful influence on the use of solid adsorbent media was the recognition that activated charcoal could be used for a very large range of organic vapors and that highly efficient recovery of those vapors could be achieved using a single solvent, carbon disulfide, which did not interfere much with gas chromatographic separation and detection when using the flame ionization detector.

Thus, it was possible to design methods for individual organic solvent vapors, even when they were encountered in mixtures with other solvents, by using the same adsorbent and analytical technique with minor modifications (e.g., adding polar modifiers to the carbon disulfide to improve desorption or optimizing the gas chromatographic column or oven temperature profile to optimize separation).

Adsorption occurs through van der Waals forces acting on molecules in pores. Activated charcoals are highly porous, with surface areas measured in many hundreds of square meters per gram, and with pore dimensions appropriate to the sizes of organic solvent vapor molecules. Activated charcoals have traditionally been used to effectively remove contaminants from water and air streams in cleaning systems; however, in air sampling they are used to trap chemicals for subsequent analysis rather than for removal and disposal. Since the subsequent analysis is the priority, any adsorbent must be able to trap molecules effectively and also be capable of giving them back quantitatively on demand. Carbon disulfide is a small molecule that can penetrate the pores of active carbon easily, and it has a very high affinity (heat of adsorption) for the charcoal surface, thus displacing the adsorbed molecules of interest. It is also a good solvent, especially for nonpolar compounds, and therefore acts as a vehicle by which they can be conveyed to the analyzer.

Activated charcoal was not the first adsorbent to be used for air sampling. Activated charcoal is a charcoal that has been heated to modify its pore structure ("activated") to increase porosity and to remove organic matter from within the pores. Silica gel was first used as it is also highly porous and available free from background contamination that could interfere with the analysis. However, silica gel has one major disadvantage in that it is highly hydrophilic (water loving). The organic molecules of interest in the air are typically present in concentrations measured as parts per million or even parts per billion while water molecules are more typically present in parts per thousand. Thus, if a sorbent shows a preference for water molecules over organic molecules, any adsorbed organic molecule will be quickly displaced by incoming water molecules, and this is the case for silica gel. Today, silica gels are still used for chemicals, such as methanol, that actually prefer adsorption in a water-rich environment, and also for some acid gases. Activated charcoals in contrast are hydrophobic (water hating) at low relative humidity, and although they are hydrophilic at higher humidity the process of water adsorption is slow and if the charcoals are stored dry before use, they do not become saturated with the first few liters of air sampled. Nevertheless, activated charcoals can still have problems with the collection of organic vapors at very high humidity and especially where high ambient temperature causes the absolute concentration of water molecules also to be high. Sample volumes should generally be reduced in these conditions to ensure efficient collection without loss of sample.

Water adsorption can cause problems with the recovery of chemicals from activated charcoal. Carbon disulfide will displace collected water but will not mix with it. Polar chemicals collected on the charcoal will partition between the two phases, and since only the carbon disulfide phase will be analyzed, recovery will be poor. Efforts to reduce this effect include adding an anhydrous salt with an affinity for water such as magnesium sulfate and adding a polar modifier to the carbon disulfide such as an alcohol. However, both techniques have drawbacks. Water molecules adsorbed onto the charcoal are also available to react with adsorbed organic molecules. For example, 2-butanone, stable on charcoal for long periods in the absence of water, is slowly converted to 3-hydroxy-2-butanone (acetoin) in the presence of coadsorbed water. Refrigeration can slow these reactions, but otherwise analysis must take place quickly. All of these issues can be minimized if an activated charcoal is selected that adsorbs ess water.

Activated charcoals are typically made from nuts (e.g., coconuts), which have a dense, yet porous structure. The initial porosity facilitates the activation process and he initial density leads to a hard, nonfriable product. However, if the material contains a residual content of inorganic elements, such as sodium, potassium, calcium, and magnesium, these act as sites of preferential water adsorption and possibly enhanced catalytic activity. Synthetic charcoals can be made from petroleum and the products can have the structural integrity of nut charcoals while being a more pure carbon. Some small sacrifice in total adsorptive capacity is usually not a problem. One synthetic activated charcoal is commercially available under the trade name Anasorb 747, and it has been used in many of the newer methods being developed, and can possibly be used in some of the earlier methods where coconut shell charcoal has been specified.

Activated charcoal is an excellent adsorbent for most vapors from organic liquids. However, it does not have a large capacity for the more volatile compounds. Carbon molecular sieves are adsorbents with very fine pores, which can be used to collect vapors of chemicals such as 1,3-butadiene, acetone, and dichloromethane. Examples include the trade names Carbosieve S-III, Spherocarb, Carboxen 1000, and Anasorb CMS. However, these adsorbents cannot be used for large molecules that are excluded by size from entering the pores.

Activated charcoal is also less useful for high molecular weight compounds that are more typically solid at room temperature, such as pesticides, polyaromatic hydrocarbons, and polychlorinated biphenyls, as these molecules cannot be easily recovered from the charcoal. For these types of chemical vapors, it is more typical to select a porous polymer adsorbent. Polymeric sorbents appear similar to expanded polystyrene beads (in fact, one of the options is polystyrene). A wide range is available, varying in their surface area, polarity, and thermal stability, and they can be modified with surface functional groups. Common polymeric sorbents specified in air sampling methods include polymers with trade names such as Amberlite XAD-2, XAD-4, and XAD-7, Chromosorb 106, and Porapak (Hayesep) Q. The desorption solvent for these polymers is more commonly methanol or dichloromethane (or a mixture of the two) than carbon disulfide.

Any sorbent material (including relatively nonporous but inert substances such as glass beads, alumina, firebrick, and diatomaceous earth) can be further treated with a reactive chemical designed to specifically react with the chemical of interest. There are several advantages of this process known as derivatization. A very volatile compound can be converted to a less volatile product. A very reactive compound may be converted to a more inert form. A poorly analyzable compound can be converted to a form more easily separated from others or to a form more readily detected. There are many examples of this, of which one of the most common is the reaction of formaldehyde with 2,4-dintrophenylhydrazine, which achieves all of the above aims. Disadvantages of this technique include a potentially short shelf life for the treated sorbent and a likely lower maximum flow rate for sampling in order to ensure complete reaction. Sometimes, the sampling substrate is coated with a less reactive material, such as a mineral acid, to enable collection and retention of difficult substances such as amines.

3.1.4 Active Adsorber Samplers The most common type of active samplers for gases and vapors are glass tubes containing adsorbent sampling media. Depending on the amount of sorbent, these tubes can vary in internal diameter from 4 mm (or even less) to 10 mm (or even more) and in length from 15 mm upward. They are sealed at the ends, normally by flame sealing, but sometimes with plastic or metal caps, and they are opened by the industrial hygienist at each end just before use. The sorbent inside is held in place by glass wool or polyurethane foam plugs. Often, these tubes contain two beds of sorbent, one acting as the primary collection section and the other acting separately as a check to confirm efficient collection and retention by the first section, that is, to show that breakthrough has not occurred. The second section is known as the backup section and usually contains half the sorbent material found in the front section. The sampling tube is used with the large front section facing forward and the smaller backup section located nearest the sampling pump. The sorbents are typically produced in beads or granules of around 0.75 mm diameter (20/40 mesh) that is a compromise between adequate contact area and low-pressure drop across the tube, although finer mesh sizes do exist, and these normally require lower flow rates for sampling. The time available for a molecule passing through a 10 mm thick bed of granules at a flow rate of 0.2 L/min is very short, yet more than adequate for complete adsorption. In fact, charcoal tubes can be used at flow rates up to 1 L/min where necessary, although such flow rates would not be advisable for most other sorbents. In method validation, the capacity of the sampler is called the breakthrough volume and it is determined as the maximum volume that can be sampled before the front section of the sampling tube begins to overload, and as a rule of thumb, that volume is relevant to any reasonable combination of flow rate and sampling time. Thus, if a sample is required for a shorter time a higher flow rate can often be used. Wherever possible, methods are validated so that a single sample can be taken over 8 h (although 4 h is also reasonable with separate samples before and after lunch). This provides a sample result that can be compared with an 8 h time-weighted average limit value. Shorter maximum time periods, such as 1 h, are used in methods where sampler capacity is an issue. In these methods, it is likely that very low flow rates are already being applied. More samples must be taken when these methods are used to monitor an 8 h period and there is a consequent increase in analytical costs.

The OSHA Versatile Sampler (OVS) is an air sampling device that contains a filter followed by an adsorbent bed in the same tube that is intended to capture any volatile material that is stripped off the filter. It has been shown that small aerosols can penetrate sorbent tubes, but that they are efficiently collected by a filter.

Granular sorbents are not the only support available for chemicals where collection is by reaction or derivatization. Filters can also be used. These are usually glass fiber filters that can be loaded with large quantities of chemicals. The advantage of a filter is that higher flow rates (1–2 L/min) can be used, and particles are also captured. Sometimes, prefilters are used before sampling tubes to remove particles, but if it is wished to sample and analyze particulates, a compromise involving sampling rate is necessary and it is not always optimal. An alternative is to use a diffusion denuder followed by a filter. The interior of the diffusion denuder is coated with a sorbent or reacting chemical, but these samplers typically have low capacity, are only rarely seen, and have not been generally promoted as standard methodology.

3.2 Diffusive Sampling (14)

Diffusive or passive sampling has become very popular as an alternative to sampling using pumps. This in part reflects the burden of pump purchase, maintenance, and calibration and in part the greater acceptance by workers who do not have to wear sampling pumps. These samplers utilize Fick's law of gaseous diffusion to control the sampling process into a collection medium. Fick's law states that diffusion across a defined geometry is at a rate defined in part by the ambient vapor concentration. Thus, if all other components are fixed, the ambient concentration can be extracted from the mass collected. Air movement at the sampler inlet has been shown to have a significant effect on the performance of diffusive samplers. Of particular importance is the fact that diffusive transport rather than air transport controls the movement of molecules into these samplers, and the diffusive pathway should be open to molecular movement yet closed to turbulent air movements, and this is usually accomplished by a porous windscreen across the face of the sampler. Another condition necessary to the performance of diffusive samplers is that there must be some minimum air movement outside the sampler so that the concentration of analyte molecules is not depleted by sampling. Movements of the person being sampled and normal workplace air movement are generally considered to be adequate for this purpose. Care must be taken to ensure the face of the sampler is not obscured, for example, by hospital operating room gowns, and that the sampler is not placed in an area where there is extremely limited air movement.

The uptake rate of a diffusive sampler is a function of the diffusion coefficient of the gas or vapor, which can be measured directly or modeled. However, it is different for each different molecule and this is the fundamental difference between passive and active sampling, where in the latter the same flow rate applies to all chemicals sampled. The uptake rate is also a function of the geometry of the sampler. Most diffusive samplers that use solvent desorption have large frontal areas and short path lengths to maximize uptake to ensure analytical sensitivity, and some of them resemble badges and are known as "badge-type" samplers. In contrast, some diffusive samplers that use thermal desorption tend to have smaller frontal areas and longer path lengths with lower uptake rates to ensure they do not become overloaded with sample. These resemble tubes and are known as "tube-type" samplers. The dimensions for the uptake rate for both sampler types are often expressed in volume per unit time (e.g., mL/min), exactly like the flow rate of a pumped sampler, although it is important to recognize that air does not pass through diffusive samplers. Thus, the major information required of the person taking the sample is simply the start and stop time of sampling, making them very easy to use. However, the diffusion coefficient is a function of both sampling site barometric pressure and temperature (temperature raised to the three-half power) and these effects become significant, for example, at high altitude or when sampling in extreme conditions. For most accurate measurements, the user should therefore also report the barometric pressure and temperature at the sampling site (uncorrected station) to the laboratory. Some diffusive samplers are available that develop a color proportional to concentration. These can be very useful in improving workers' awareness of hazards.

It is essential for the sampling medium to be an efficient sorbent for the sample molecules because if the concentration at the sorbent face is not effectively zero, reverse diffusion can become an issue. Practically, any of the solid adsorbents used for active sampling tubes can be used in commercial diffusive samplers, with the activated charcoal most commonly used with solvent desorption. Where thermal desorption is used, porous polymers or graphitized carbons are often the sorbents of choice. Liquid absorbing media can also be used, but these devices are uncommon today. If a reaction is the preferred method of collection, the reacting chemical can be coated or impregnated on a substrate and this is easier to handle than a solution of the reagent.

Corroborative testing of diffusive samplers for mercury, nitrogen oxides, ammonia, hydrogen sulfide, formaldehyde, and other organic vapors has been performed and comparison of results to reference methods has in many cases shown excellent agreement. However, for many years their widespread use was limited by a lack of acceptance by the industrial hygiene community. In recent years, this situation has changed partly due to the validation and publication of diffusive sampler methods in OSHA validated analytical methods.

4 SAMPLE ANALYSIS

4.1 Solvent Desorption

Using a solvent to recover collected molecules for analysis is the traditional and the most common method of analysis. The sorbent is simply transferred from the sampling tube into a vial in the laboratory and solvent is added. Sometimes, the desorption process involves agitation or some minimum contact time or both. Typically, the ratio of the solvent to sorbent medium is about 1 mL of solvent to 100 mg of sorbent material. The solvent can cause problems if it or any contaminant of the solvent interferes with the analysis, for example, by coelution during separation or by reaction with the collected analyte. Solvent desorption also reduces sensitivity because only a fraction of the sample is analyzed. Finally, if the desorption solvent is present in the sample it cannot be measured in the desorbed sample. As already noted, carbon disulfide is the traditional solvent for activated charcoal and, as also noted, this can be a problem for polar compounds collected from humid environments. The efficiency of recovery is known as the desorption efficiency and it must always be tested as part of the method validation, with each change in the lot of sorbent, and with any significant change in the analysis or reagents. Each laboratory must determine its own desorption efficiency to account for differences in techniques and analytical policies. A known amount of the chemical of interest is applied (spiked) on the mass of sorbent in the front section of the sampling tube, the spiked samples are usually allowed to equilibrate overnight, and the solution is desorbed and analyzed. The desorption efficiency is normally determined over a range of concentrations using separate spiked samples. Typically, the recovery is slightly less than 100% but preferably more than 90%. It is normally constant with the mass of the chemical of interest so that a single desorption efficiency correction factor can be applied to sample results. However, recovery is sometimes observed to fall off as the mass of the chemical of interest gets smaller, and then a correction curve must be constructed and applied. Desorbed samples can be reanalyzed to determine if there are stability issues for desorbed samples. If there is any indication that coadsorbed chemicals, including water vapor, may affect the recovery, desorption efficiency should be retested with sorbent that is preconditioned accordingly. The desorption efficiency, especially for polar analytes, should be determined at the mass loading that is equivalent to the exposure limit from sampling medium that has been prewetted by sampling contaminant-free humid air.

4.2 Thermal Desorption

A serious drawback of recovering adsorbed gases and vapors by liquid desorption is the dilution of the sample that results. It seems counterintuitive to do this after collecting the molecules of interest by concentration on a sorbent bed. All the disadvantages of using a solvent for desorption disappear with a technique known as thermal desorption. In thermal desorption, the sample tube is heated to remove the chemicals of interest as vapor in an inert purge gas. The chemicals are then recollected on a much smaller bed of sorbent (which does not have to be the same as the sorbent in the sample tube), which is typically held at reduced temperature (generally about −30°C). This second tube can then be heated very quickly to transfer the chemicals of interest directly into the gas chromatograph for analysis. This process is sometimes called cyrofocusing. This procedure allows the entire sample to be injected into the gas chromatograph in a small plug but without dilution by a desorption solvent. Techniques are available to handle water vapor collected in the sample, and the judicious use of "splitting" the sample flow allows the operator to inject more or less of the sample as desired. Split recollection on another sorbent bed is available on some instruments so that the analysis is not "one shot." The one-shot analysis is a disadvantage that has been cited as a reason preventing widespread acceptance of hermal desorption techniques.

Activated charcoal and silica gel cannot be used as sorbents for thermal desorption because the very high temperatures necessary to remove trapped molecules would also destroy the molecules. Porous polymers or graphitized carbons are used instead, either singly or in combinations. The range of alternatives is large and validation of heir use has been slow to accumulate. Tenax is the trade-name for a polymer commonly used in relatively unpolluted environmental situations, while Carbopack X is the trade-name for a graphitized carbon that has been used in more polluted nvironments. The high sensitivity possible when the entire sample is available for nalysis makes this technique very attractive for environmental and indoor-air quality nvestigations. However, the lack of a backup section to confirm complete collection has been another hindrance to acceptance of this very sensitive method of analysis. The absence of methods published by the government results in a lack of interest by the hygiene community generally, but this has been changing. Some government-published methods exist in the United Kingdom, and many laboratories in the United States are now able to offer analysis by thermal desorption and gas chromatography.

4.3 Gas Chromatography (15)

Gas chromatography is a physical process for separating components of complex mixtures and it is the most common analytical technique used routinely for gases and vapors. A gas chromatograph has the following components:

- Carrier gas supply complete with a pressure regulator and a flow controller;
- Injection system for the introduction of a gas or vaporizable sample into a (usually heated) port at the front end of the separation column;
- Separation column containing a stationary phase consisting of either an inert solid material, used alone as in gas–solid chromatography or as a support for a thin layer of a liquid substrate, as in one type of gas–liquid chromatography, or simply an internal coating of a liquid or a bonded phase on a fused silica capillary column;
- Heater and oven assembly to control the temperature of the column(s), injection port, and detector unit;
- Detector, of which several are available;
- Recorder or data system to store and manipulate data.

Separation of volatile molecules is based on the affinity of the sample components for the solid or liquid materials of a particular column, the flow rate of the carrier gas, and the operating temperature of the column. Improved separations are made possible by the use of temperature programming. The system is optimized so that the sample components elute from the separation column one at a time in distinct bands that are usually called chromatographic peaks; thus, they evoke separate responses by the detection system. The detector response of the peak is usually proportional to the concentration of the eluted sample component. The time that each sample component is retained on the separation column is called the retention time and it can be used to provisionally identify peaks when compared to retention times for separate solutions containing known pure substances suspected to be in the sample that are analyzed under identical conditions. This provisional identification can be confirmed by an appropriate match of retention time on another column with a different chromatographic phase or by an appropriate spectrum from a mass selective detector. Calibration is performed by injecting known mixtures of the pure substances contained in the desorbing solvent (solvent desorption) or with sorbent tubes containing known mixtures of the pure substances (thermal desorption). The most common detector used for gases and vapors is the flame ionization detector. Other detectors that are highly sensitive to specific classes of compounds such as the electron capture detector, flame photometric detector, or thermionic (nitrogen–phosphorous) detector are also in general use. Less volatile compounds can be made more volatile by derivatization, and thus they can be analyzed by a gas chromatograph. Alternatively, less volatile chemicals can be analyzed by high-performance liquid chromatography or by some other technique.

5 METHOD VALIDATION (16)

The ratio of the amount of contaminant entering the sampler to the amount recovered for analysis known as collection efficiency. Collection efficiency is best determined by using the device to sample a dynamically generated controlled test atmosphere containing the contaminant during laboratory validation tests for the sampling and analytical method. It is usually calculated using the known theoretical concentration of the test atmosphere and the amount of contaminant recovered after analysis. If recovery from diffusive samplers is quantitative, collection efficiency experiments can be used to determine the sampler uptake rate for the contaminant in the test atmosphere.

It is essential that a method selected for workplace air sampling provide results that are fit for their intended purpose, especially where they will be used to make decisions regarding workers' health or the investment of considerable financial resources in control measures. Requirements for the performance of sampling and analytical methods have been published in the United States and in Europe, and method validations are geared toward testing procedures to these requirements. However, each validation protocol is different from the others, particularly in terms of the limits of testing. For example, one protocol may only suggest testing at room temperature, another might suggest extremes of 5 and 35°C, while yet another (particularly in the armed forces where outdoor exposures in extreme climates may be possible) might suggest a wider range, such as from −20 to 45°C. All such protocols are relevant to selecting a sampler for use at 25°C, but extrapolation requires caution. The GESTIS database ranks published methods for each substance based on the thoroughness of the validation, which can be a useful guide.

6 QUALITY ASSURANCE AND LABORATORY ACCREDITATION (17)

All sampling and analytical methods have some degree of uncertainty. The total uncertainty depends on the combined effects of the contributing uncertainties inherent in sampling and analysis. Sampling uncertainty for pumped sampling is generally assumed to be 5% and it is attributed to sampling pump error. Analytical error can be estimated through analysis of quality control samples in a laboratory quality assurance program. If the variances for sampling error and analytical error are homogeneous, they can be combined by the pooling the variances. The pooled variances can be further manipulated to produce a single number for each substance to estimate sampling and analytical error. The overall goal of the program is to provide the industrial hygienist with a statistical tool to compare analytical results with exposure standards or other threshold limits. Each laboratory must establish its own quality control program and generate its own quality control data.

Another purpose for laboratory quality assurance is to establish and maintain laboratory accreditation within the facility. The objective of accreditation is to establish a laboratory quality system that will ensure the high quality of sample results through the services of qualified personnel in a well-equipped laboratory using established and tested analytical methods. The industrial hygienist should initiate dialogue with the analytical laboratory before beginning a sampling campaign and seek guidance for analytical method selection. Such dialogue will also determine the suitability of the laboratory and whether the laboratory is accredited for the analysis. Field personnel should be part of the quality system and are responsible for maintenance and calibration of their equipment; they must provide appropriate documentation regarding sample identities, sampling times, flow rates, comments and records of environmental conditions, and the appropriate numbers of field blank samples from the same medium lot number as used for sampling. The industrial hygienist can prepare or purchase known samples (e.g., old sets of proficiency test samples or certified reference materials) that can be furtively submitted to the laboratory along with field samples as independent checks on the analysis.

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