Review

Sorbent trapping of volatile organic compounds from air

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Abstract

The use of sorbents in trapping volatile organic compounds in air for subsequent analysis is reviewed. Sorbents are classified in accordance with the mechanism used to recover the trapped compounds, either solvent or thermal desorption. The use of sorbents is contrasted with other sampling procedures, such as collecting whole air samples using canisters. New developments such as solid-phase microextraction are described. In particular, emphasis is placed on a holistic approach to sampling and analysis, and communication is encouraged between those who take samples in the field, and those who perform the analysis.   © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Volatile organic compounds (VOCs) are compounds normally present in the vapor phase at room temperature [vapor pressure greater than 0.1 mmHg (0.0133 kPa) at 25°C] [1]. Compounds less volatile are known as semi-volatile organic compounds (SVOCs). SVOCs may be present in the atmosphere in the vapor phase, but are more normally associated with aerosol, either as dusts or liquid droplets. There may be several reasons to trap VOCs from the air, one of the most obvious being to clean the air, for example in the recovery of waste anaesthetic gases in hospital surgeries. This review will cover only the trapping of VOCs for their subsequent analysis, in order to evaluate air quality. Measurement of the concentration of VOCs in air is necessary for many reasons, in order to determine the sources and transport mechanisms of pollution, for health effects studies, and to determine compliance with regulated limits. The concentration of VOCs in air can fluctuate in both time and space, and measurement techniques must be designed to accommodate these fluctuations and to provide a result which can be used for the intended purpose. Measurements may be designed to detect maximum concentrations (or at least concentrations in excess of a limit value), or concentrations averaged over a specific time period. One method is to use near real-time instruments, such as infra-red spectrometers or portable gas chromatographs or their detectors. However, these instruments have limitations of cost, stability, field calibration and power supply which may detract from their use. Another method, which solves many of these problems, is to take a sample in the field and send it to a laboratory for analysis. The integrity of the sample must be preserved through the trapping, transportation and analysis stages [2]. Whole-air samples collected in evacuated canisters or polymer bags are often used, but collection of only the VOC portion is possible by trapping on a sorbent medium. The collection of VOCs by solid-phase extraction (adsorption or reaction with a solid substrate) is covered in this review. Where similar methods are used for the collection of inorganic gases and vapors this is noted, but not covered in detail.

Much of the impetus for air analysis came from the practice of industrial or occupational hygiene. Only later did interest shift to the ambient environment and the control of pollution. When it became known that the high concentration of solvent vapors found in many industries may be potentially or actually harmful, measures were taken to protect workers from the effects of exposure to these chemicals. Legislation such as the Occupational Safety and Health (1970) Act in the USA was put in place requiring the control of workers exposure to airborne toxic chemical hazards. Therefore, many methods of air sampling and analysis were developed originally to sample part per million concentrations averaged over 8-h work shifts, using equipment that was lightweight and unobtrusive so that it could be carried easily and yet would sample from the workers' breathing zone. This is the principle still in use today for occupational hygiene sampling. Guidance is available concerning the selection of an appropriate sampling strategy for determining workplace exposures [3]. Small battery-powered air pumps are attached to the belts of workers and the inlets of the pumps are connected by flexible tubing to a tube containing a sorbent material attached to the lapel of the workers shirt. The pumps pull air at a fixed, calibrated flow-rate through the sorbent tube [4,5]. The VOCs of interest are extracted from the air by adsorption or reaction with the sorbent surface. At the end of the designated sampling period the pump is switched off and the start and stop time and flow-rate are recorded. Typically the flow-rate has

been calibrated at least at the beginning and end of the sampling period, if not more often, and so the total volume of air sampled can be recorded. The sorbent tube is then capped and sent to the laboratory for analysis, after which the total mass of each VOC is divided by the air volume to give the concentration in mass per unit volume from which the volume ratio concentration can also be calculated. This same principle of sorbent trapping of VOCs in air has been applied to sampling relatively less polluted ambient and indoor environments [6], with some advantages and disadvantages over whole-air sampling using canisters. For any type of sampling exercise, it is possible to make choices in the type of sorbent material used, the method of sampling (pumped or diffusive, see below), the method by which the trapped vapors are removed (or not) from the sorbent for analysis, and the method of analysis. Different techniques may be more or less applicable depending on whether the measurement period is short or long-term, the concentrations are high or low, and whether the sample is meant to be personal or site-specific.

The final choice includes these factors as well as considerations of cost and the required accuracy of the result. For example, a method may be selected because the laboratory has a preferred analytical finish, or because the background of one sorbent type is appropriate to the measured concentration, or because of regulatory requirements, or the choice may be related to any of the other considerations mentioned. It is often the case that more than one method could be considered to give a ''true'' measurement. In this review sorbents are classified in the first instance as to their method of trapping (physical adsorption or chemical reaction). Further, adsorbents will be separated according to their principle mechanism of desorption (solvent or thermal). Finally specific consideration will be given to the features of sorbents important for their use in diffusive sampling. Where analytical considerations are important in the choice of sorbent these will be described.

2. Validation of sampling methods

Many air sampling methods are developed for purposes of regulatory compliance. Regulation may be based on prevention of acute outcomes or chronic diseases, but may also be for purposes relating to the quality of life, for example to prevent irritation. Underestimation of exposure may result in an erroneous assurance of safety or not uncovering correlations between exposure and ill-effects, while overestimation may result in costly and unnecessary remedial actions. Official government methods as well as those promulgated by standards organizations and private laboratories are generally validated; that is to say they have been evaluated by testing in accordance with some defined experimental protocol that covers the range of environmental conditions under which the method will be used. In general, all published protocols (e.g., Ref. [7]) address the same issues, although there is often variation in the experimental procedures and the exact range of conditions, and in the assessment of the results. Attempts are being made to harmonize these protocols across the world, but there are still some obstacles to overcome. For example, one obvious distinction is between the room temperature in the USA (25°C) and that in Europe (20°C). The accuracy requirement generally imposed on industrial hygiene measurement methods in the USA is ±25% (at the 95% confidence limit). The corresponding requirement for methods of the European Union at concentrations around the limit value is ±35%. Sources of published methods are listed in Refs. [8–16]. In some cases it is possible to download the methods directly from the appropriate web-site. Many more may be found in corporate industrial hygiene or environmental departments. Although often unpublished, some are available through the Methods Exchange Network of the American Industrial Hygiene Association (Fairfax, VA; www.aiha.org). Reviews are also published [17].

3. Trapping by adsorption

Adsorption is a surface phenomenon and the amount of surface available for adsorption is critical [18,19]. Not all of the sorbent surface is available for adsorption, particularly when the surface of the sorbent is microporous, as molecules might be too large to enter the pores (this is known as the ''molecular sieve'' effect). Since the amount of surface is related to the porosity of a material,

sorbents with very high surface areas tend to have pores on the order of molecular dimensions. Pore-sizes have been classified by IUPAC as macropores (>50 nm diameter), mesopores (greater than 2 nm but less than 50 nm diameter), and micropores (<2 nm diameter). Taking an adequate sample of air for analysis involves collecting large numbers of molecules on the sorbent, so that pore-filling mechanisms become important. Macropores are filled by mono-molecular coverage (monolayer) followed by the accumulation of further layers (multilayer adsorption). Adsorbed molecules are in a condensed phase which more closely resembles a liquid than a vapor and Henry's Law can be used to describe this situation. Initial work on the use of sorbent materials for trapping environmental components of air used the liquid coatings popular in gas–liquid chromatography where Henry's law applies [20]. The solid sorbent materials used in gas–solid chromatography showed greater adsorptive capacity and quickly became more popular [21]. It was assumed that the concentrations of VOCs in air were sufficiently low that when molecules were adsorbed on these sorbents a condition of extreme dilution would exist similar to the case of gas–solid chromatography, so that the adsorption could be described by the linear portion (Henry's Law region) of the Freundlich isotherm, and retention volumes could be used to predict safe sampling volumes [22–24]. However, the concentrations found in polluted environments lead to adsorption behavior that is better described by the curved portion of the Freundlich isotherm, or by the Langmuir isotherm, where breakthrough is a function of concentration [25–31].

Filling of micropores is fundamentally different. Adsorbed molecules are close to more than one wall of a pore and are thus held by stronger forces. The close presence of other adsorbed molecules enhances the adsorption effect. Instead of a diffuse transition from a non-adsorbed to a desorbed state there is a meniscus formed, and hence microporous sorbents are defined better by their pore volume than by their surface area. This is important as surface area measurements above 1000 m^2 g^{-1} tend to be related more to the method of measurement than the true surface seen by the adsorbate molecules. Unfortunately, very few pore volume measurements have been made on the kind of sorbents used in air

sampling. Pore shape may also influence the filling mechanism as some pores have openings smaller than the internal part of the pore. Activated charcoals, zeolite and carbon molecular sieves, and silica gels used in air sampling procedures are typically microporous. Adsorption in micropores can be modeled using the Langmuir or Dubinin–Radushkevich equation.

The kinetics of adsorption are such that almost complete removal of molecules from an air stream can be accomplished with a small bed depth of appropriate sorbent, despite high linear flow-rates through the bed [31,32]. If sorbent bed depth (or mass) is graphed against breakthrough volume (the volume of contaminated air passed at constant concentration before the analyte is detected in the outlet stream, see below), the linear portion of the relationship can be extrapolated to the x-axis to give the so-called "minimum bed depth", below which breakthrough would be instantaneous (in actuality the line curves to intersect the origin) [31,33]. Even a small bed (e.g., 100 mg charcoal in a 4 mm inside diameter tube) normally exceeds this minimum bed depth by a factor of three or more [33]. Thus the technique of sampling by adsorption is perfectly suited for personal sampling, where an unobtrusive device is required. Sorbent tubes are typically 70–150 mm long×4–10 mm diameter, depending on the quantity and density of the sorbent. The complete assembly of tube and holder weighs only a few grams. The holder is clipped to the person's clothing in their breathing zone, or a suitable harness, and connected to a pump with a length of flexible tubing. The pump is fixed to the wearer's belt or harness.

4. Back-up sections and breakthrough

Additional sorbent beds may be placed behind the primary bed to guard against breakthrough. Breakthrough is the appearance of sampled molecules in the outlet stream, either because of saturation within the bed, or displacement by another chemical. Sampling is no longer efficient when this occurs, and, as breakthrough progresses, the sample will be less and less representative of the external environment. Over a wide range of flow-rates, breakthrough is indepen-

dent of flow-rate, depending only on the total volume of sample passed [31,32]. However, as noted above, breakthrough is dependent on concentration, and also on temperature, and the presence of other species in the atmosphere [34,35]. Practical tests of breakthrough with constant atmospheres at or above the target value are preferred [7,29–31,36]. Where concentrations are high this is possible using a standard gas chromatography (GC) system, or other detectors, connected to the outlet of the sampler. When concentrations are low, more elaborate detection methods are required [29]. The breakthrough volume is adjusted by an additional safety factor (usually reduced by one-third) to account for the presence of other chemicals in the environment. One particularly common interfering chemical is water vapor. High humidity can dramatically affect breakthrough volumes on hydrophilic sorbents such as silica gel or charcoal (which is nominally hydrophobic but becomes hydrophilic at high humidity [37]). For best results, breakthrough determinations should be carried out with humidified air. The alternative approach to determining breakthrough (extrapolated chromatographic retention volumes) suffers from being unrealistic as the effects of high concentrations and the presence of competing vapors (especially water vapor) are not taken into account. Although these retention volumes are reduced by a greater safety factor (50%), this might still not be enough to ensure breakthrough does not take place. In a study of the performance of different sorbent materials [38] the two approaches were compared for a very few sorbent/VOC combinations, with the conclusion that the results were comparable, but in this study the direct method employed concentrations of only 1 mg m^{-3}, so the test was not strictly relevant to the concentrations encountered in many occupational hygiene or polluted environmental situations. Attempts have been made to model breakthrough [19,30] using the same equations that have been used to model the breakthrough of contaminants in respirator cartridges [39–41], with some predictive success. In addition to the references already given, other breakthrough volume measurements by both direct and indirect methods have been published [42–46]. Another source is published, validated methods. However, the use of back-up sections is still the normal method of guarding against sorbent

saturation, particularly in occupational hygiene sampling.

The second section of sorbent bed known as the back-up or secondary section can be used to guard against breakthrough in field situations. The notional point of breakthrough is an outlet stream concentration equal to 5% of the inlet concentration. At this point the amount of the total sample which would be found on the back-up section normally is insignificant. Some studies report breakthrough as the point at which 5% of the total sample is found on the back-up section, although this is actually equivalent to an outlet concentration well in excess of 5% [28]. This is an important distinction, but one not always made in method evaluations. The back-up section will continue to sample effectively even beyond this point. The limit at which sampling by both the front and back-up sections becomes inefficient is when the percentage of total sample in the back-up section exceeds 20–25%. Therefore it is common practice to add the two sections' results together if the back-up section is less than 15% the total sample. When the back-up section contains 33% of the total sample saturation has occurred. The relationship between breakthrough and the amount of material found in the second section is illustrated in Fig. 1. If sample displacement has taken place, for example, because of high humidity and the collection of large quantities of water vapor, it is possible for the back-up section to contain more than 33% of the total sample.

5. Trapping by reaction

Sorbents are also sometimes used as supports for chemicals which can react with specific analytes to form a more stable or more easily analyzed derivative [47–49]. The kinetics of reaction may be slower than those of adsorption, so that slower flow-rates or larger sorbent beds may be required to increase contact time and ensure complete reaction. Where kinetics are fast, the derivatizing agent or other reacting chemical may be impregnated on a filter, allowing higher flow-rates to be used. Sorbents may also be used as supports for the color reactions used in detector tube technologies. These sorbents often have large, open pores to facilitate reactions, examples include Florisil, Chromosorb W, etc. A more
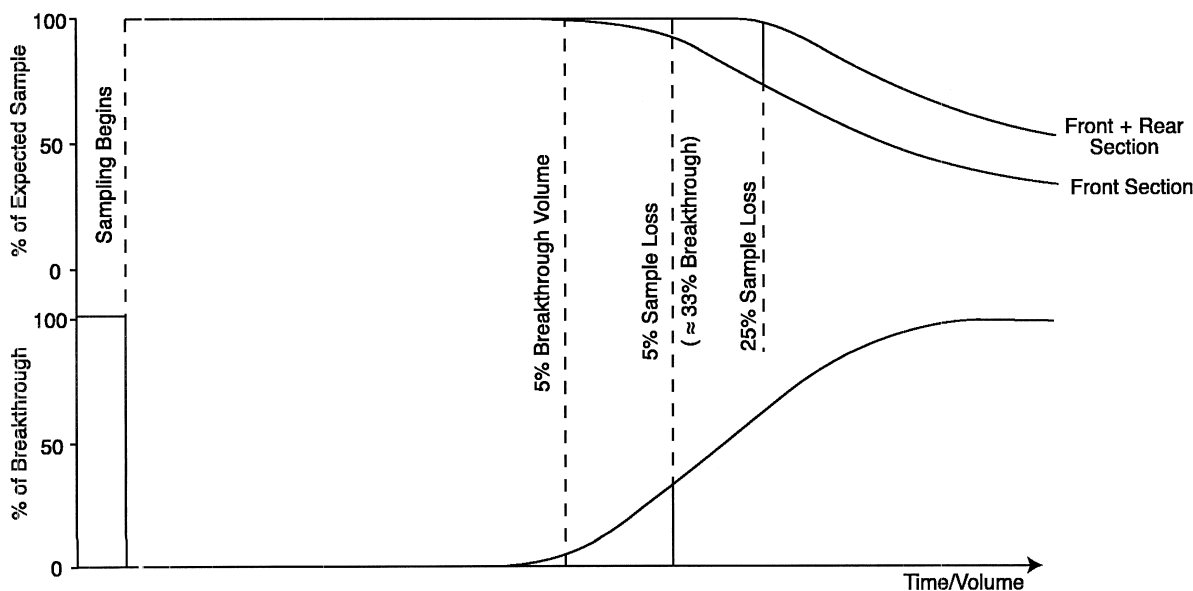
Fig. 1. Relationship of breakthrough to sample loss in a typical two-section sample tube sampling an atmosphere of constant sorbate concentration, showing the difference between 5% breakthrough volume and 5% sample loss to the back-up section. Actual shape of the curves will vary with sorbent, sorbate, concentration, temperature and the presence of other sorbates.

porous sorbent is used to increase the loading of chemical, or to ensure the adsorption of the reaction product. It may also be possible that reaction energies are lowered by the environment of the adsorption site. Reaction products may be amenable to thermal desorption (see below), but excess of reagent may cause problems, and solvent desorption (see below) is far more common. The most common reaction in use for trapping VOCs is that between 2,4-dinitrophenylhydrazine and carbonyl compounds with high-performance liquid chromatography (HPLC) analysis [50–54]. Alternative methods have been proposed to allow analysis by GC rather than HPLC [55–57].

6. Solvent desorption

Where GC is used as an analytical technique, it is necessary to inject the sample onto the chromatographic column, and liquid injection with a manual or automatic syringe is the most common procedure. Evaporation of the sample takes place within the heated injection block, and the sample enters the column in the gas phase. When air samples have been obtained by trapping on a solid sorbent, it is necessary to desorb them with a liquid solvent, suitable for injection into the chromatograph [58]. The solvent to analyte ratio will be about 1000:1 or more so it is important to choose a solvent that will not interfere with detection of the analyte(s). The solvent must also be capable of stripping the analyte(s) from the sorbent with a high degree of efficiency (NIOSH method requirements are >75% [7]), but, more importantly, with a high degree of reproducibility. A solvent that is particularly suitable for hydrocarbon analysis is carbon disulfide [59–61]. It has a high heat of adsorption on activated carbon, displacing other molecules. Some very volatile molecules may be vaporized during this procedure and chilled desorption or special equipment, such as a "vial-within-a-vial" [62] is recommended when analyzing these very volatile compounds. Carbon disulfide is a good solvent for non-polar compounds. It elutes rapidly at the front of the analysis on most common GC columns, and has a very low response on a flame ionization detector. This combination of qualities has made carbon disulfide the most popular solvent for this kind of analysis. However, it can react with certain compounds (e.g., amines), and can

interfere with the analysis of certain volatile chlorinated hydrocarbons. Carbon disulfide is not suitable for electron-capture detectors. It is highly toxic and has an objectionable odor.

The desorption efficiency of analytes from charcoal using carbon disulfide depends on the type and quantity of analyte, the types and quantities of other collected chemicals, especially water vapor, the amount of sorbent, and the amount of solvent [63–68]. Analyte behavior can be broken down into several broad classes. The first type includes chemicals which are neither particularly polar nor reactive. Toluene is a good example, although it is one of a minority of chemicals that exhibits virtually complete recovery over the entire range of analyte/sorbent and analyte/solvent ratios normally encountered. Other compounds in the same class include hexane and 1,1,1-trichloroethane, but these compounds exhibit poor recovery at very low ratios of analyte/sorbent, and the reason for this behavior is not clear. It may be the result of irreversible sorption, or simply a kinetic effect of molecules trapped in bottle-neck pores. Dehydrohalogenation has been observed with some chlorinated species. Typically, compounds in this class exhibit near perfect recovery over most of the loading range, and this is unaffected by the presence of other compounds, including water vapor.

The second class of behavior is exhibited by relatively non-polar, but more reactive compounds, especially those with a labile double bond (e.g., styrene, vinyl acetate, ethyl acrylate or 1,3-butadiene). These compounds tend to show good recovery at high loadings of the compound per unit mass of charcoal, but the recovery falls off rapidly to very low values (10–30%) as the loading decreases. For example, on a 100 mg charcoal tube, the recovery of styrene falls from near 100% at 1000 µg loading to less than 20% at 50 µg loading [69]. The behavior is a function of analyte/solvent ratio as well as analyte/sorbent ratio, although the interaction is not simple, and may be modified further by the presence of water vapor, since some of these compounds are slightly polar. Recovery can be improved by using more solvent as well as by using smaller beds. However, analytical sensitivity is sacrificed in the first case, and breakthrough is compromised in the second. Recovery varies also with

carbon type, for example, this behavior is less pronounced with petroleum-based charcoals than with coconut charcoal, and may also be improved by the presence of free-radical inhibitors such as hydroquinone [70], or *tert*.-butyl catechol (e.g., OSHA methods 56 for 1,3-butadiene, 89 for styrene and divinylbenzene, and 92 for methyl acrylate and ethyl acrylate). These observations indicate a polymerization reaction may be involved. Only a few select sites on the charcoal surface are implicated, as the long-term storage stability of the unreacted portion of the analyte is often good. However, once desorbed and in carbon disulfide solution, compounds such as styrene and 1,3-butadiene are no longer stable and tend to disappear rapidly.

Polar compounds, such as alcohols, are poorly soluble in carbon disulfide, and generally prefer to associate with other polar molecules, and especially with water. Water adsorbed on a charcoal surface is usually located in discrete clusters, to which polar molecules may hydrogen-bond. This is shown well by the behavior of methanol on Anasorb 747, where the capacity for methanol increases as more water is adsorbed at high humidity (OSHA Method 91). Should sufficient water be adsorbed, carbon disulfide will displace it as a discrete phase into which polar molecules will partition where they will generally be lost to further analysis. One method of dealing with this is to use a two-phase carbon disulfide/water desorbing solvent and to analyze both phases [71]. Reducing the quantity of charcoal increases recovery, not only by increasing the analyte/sorbent ratio, but also by reducing the amount of water adsorbed. Uptake of water by charcoal is kinetically slow at room temperature, and saturation of a 100 mg bed normally requires the passage of about 20 l of humidified air, so that reducing the air volume will also reduce the amount of water collected. Presample air-drying tubes can be used, or a drying agent may be added to the desorption solvent. However, in the first case VOCs may be adsorbed and lost [72], and in the second case fine particles from the drying agent can block syringe needles or injection ports. Polar compound recovery is improved if a polar co-solvent is added to the carbon disulfide. Higher alcohols are preferred [73], as methanol and ethanol may react with carbon disulfide [74] (although this was not observed in the

OSHA validation of methods for methanol, Method 91, and ethanol, Method 100, where carbon disulfide is used with dimethylformamide as a co-solvent). Isopropanol, butanol, amyl and hexyl alcohols have been used for this purpose. Dimethylformamide, either alone [75], or in combination with carbon disulfide (OSHA Methods 91, 100), is quite popular. Its high boiling point (172°C) means that it tends to elute in an area of the chromatogram with little else; it is a good solvent for polar compounds and a reasonable solvent (usually better than 80% recovery) for non-polar compounds. Its low vapor pressure means it is less of an inhalation hazard, although it can be absorbed through the skin. Mixtures of carbon disulfide and dimethylformamide can be unstable in the presence of moisture, for example, when desorbing samples collected at high humidity. A mixture of methylene chloride–methanol (95:5, v/v) is also popular [64], and a mixture of dimethyl sulfoxide (DMSO) and carbon disulfide has also been proposed [76]. Recovery of polar compounds also fluctuates with the quantity of other polar compounds in the sample, when a polar modifier is not present in the desorbing solvent. In general the minor component is the one most affected.

Polar compounds may also be reactive on carbon surfaces. Reactions known to occur include ester hydrolysis (e.g., butyl acetate on long-term storage [32]), transesterification (e.g., the reaction of ethyl acetate with isobutanol [77]), and hydration (e.g., acetone and 2-butanone with adsorbed water vapor [33]). Note that the reaction of ketones requires the presence of water vapor, and that the same compounds spiked on dry charcoal are stable for long periods. The half-life of the reaction appears to be several days, and in such instances it is difficult to distinguish recovery losses in the desorption process from recovery losses through reactions on storage [78]. In general, those factors that contribute to poor recovery that are unrelated to specific chemical reactions can be modeled by equilibrium considerations [79,80]. However, the phase equilibrium method for determining desorption efficiencies [81,82] is not a good method precisely because it does not relate to the real-life situation [83] of vapor phase collection from atmospheres of varying humidity, together with a storage period prior to desorption, when reactions take place.

In summary, there are four classes of behavior normally observed in the recovery of VOCs from charcoal with desorption using carbon disulfide. Non-polar, unreactive compounds typically show efficient recovery, unaffected by loading or the presence of other chemicals or water vapor. Relatively non-polar, but reactive, compounds show desorption efficiencies that approach 100% under certain analyte/sorbent/solvent ratios, but which decrease rapidly as these ratios become unfavorable. Deactivation of the charcoal surface improves the situation. Polar compounds often have desorption efficiencies significantly less than 100%, which can vary further with the presence of other polar species or water vapor. Polar solvent modifiers can be used to remedy this situation. Polar compounds which are also reactive (e.g., carbonyl compounds) exhibit behavior which is more complicated still, and may require a combination of charcoal surface deactivation and polar co-solvents. Some compounds may be too reactive to be sampled on charcoal at all (e.g., low-molecular-mass aldehydes).

Where the analytical finish is HPLC, charcoal is less often used as a sorbent than silica gel, and carbon disulfide is never used as the solvent. Typical solvents include methanol and acetonitrile, often mixed with water, and sometimes a buffer. Again, the sorbent may be coated with a chemical that reacts with the analyte of interest to form a product more amenable to analysis. As already noted, the commonest example of this is the use of acidified 2,4-dinitrophenylhydrazine in the analysis of aldehydes according to EPA Method TO-11A [50,51]. The hydrazone derivatives are more stable than the aldehydes and provide much greater analytical sensitivity (sub-ppb levels). One issue with sampling using coated sorbents to form derivatives is the ability of reactive species in the atmosphere, such as ozone, to attack the derivative compounds [52]. This may require the use of an ozone scrubber prior to the sorbent bed for best results [53].

7. Sorbents used with solvent desorption

7.1. Silica gel

Silica gel has been used for the determination of

non-polar hydrocarbons in air [84–86]. However, water vapor is strongly adsorbed from humid air and can displace adsorbed organic molecules. Over the years silica gel has been replaced with other sorbents; it is now used only for certain very polar organic compounds, such as methanol (NIOSH Method 2000), aminoethanol (NIOSH Method 2007), amines (NIOSH Method 2010), alkanolamines [87], and gluteraldehyde [88], as well as for some inorganic species, and as a substrate for coating with derivatizing agents.

7.2. Activated charcoal

By far the commonest sorbent, especially in occupational hygiene determinations [58,59,61,89–93], is porous charcoal where the microporosity has been enhanced by activation, typically using steam oxidation. Nut shell charcoals are particularly useful for this purpose as they are hard and non-friable, and possess an original porosity very suitable for activation. Coconut shells are the most abundant and cheapest starting material, although olive pits are sometimes used in Mediterranean areas. A drawback of using plant materials is the existence of a residual inorganic ash content.

The atoms of sodium, potassium, magnesium, calcium, etc., disrupt the regular charcoal structure and the local electrical configuration. The results are sites of enhanced catalytic activity and water uptake, and a charcoal whose adsorption and desorption properties vary with the provenance of the starting material and conditions of activation. Water uptake is a problem with activated charcoals. When the relative humidity is greater than about 50%, sufficient water is adsorbed that when further water molecules are adsorbed by hydrogen bonding to their fellows islands of water coalesce to form a water layer, and the surface becomes hydrophilic. The capacity of charcoals for water in this region approaches 30% of their dry mass. This water can displace adsorbed organic molecules, react with them (e.g., 2-butanone forming 3-hydroxy-2-butanone), or form an immiscible phase on desorption into which polar molecules (e.g., acetone) can partition and essentially be lost to analysis. Charcoals based on petroleum or by-products of the petroleum industry (such as Witcarb or JXC charcoal, and Anasorb 747, see below) contain

far less inorganic material and can be fashioned into a charcoal with very reproducible properties. However, they rarely approach the huge microporous capacity of nut-shell charcoals, and are more expensive. Charcoals made from coal also exist, but there are few comparisons of their properties with those of other charcoals used for this purpose. Coconut shell charcoal is used in the majority of NIOSH and OSHA methods, and widely in official methods in European countries. However, it is not used in EPA indoor or outdoor sampling methods, but is used extensively for direct sampling of emissions (40 CFR Part 60 Appendix A Method 18), where concentrations are potentially much higher. In some countries, charcoal tubes have been used for sampling ambient concentrations of VOCs by simply taking very large samples (40 000 l) [94].

7.3. Anasorb 747

This is a charcoal made from petroleum mixed with an organic solvent and formed into beads. Removal of the solvent leaves a regular porosity which is enhanced by activation [33,69,95–97]. The material is produced as round, hard beads in a tight size range around 0.75 mm diameter, which leads to even packing in the bed. Although it has a lower capacity than coconut charcoal, it absorbs less water for a given volume of sampled air over almost all humidities, and desorption efficiencies for polar compounds are generally higher. In addition, compounds unstable on coconut charcoal (e.g., vinyl compounds, acrylates and ketones) are more stable on Anasorb 747. Anasorb 747 is not identical to Carboxen 564 (see below), as is sometimes claimed. Anasorb 747 is used in many OSHA methods and corporate industrial methods (e.g., from Union Carbide and Rohm & Haas). It is also used in some US Environmental Protection Agency (EPA) methods for mobile source emissions [98] or in contaminated site monitoring (EPA SW846 Method 0031).

7.4. Carboxens

The range of sorbents called Carboxens are manufactured from the partial to full carbonization of porous polymers. By careful process control, a range of properties can be produced. The most commonly

encountered is Carboxen 564, which has a high porosity, and which is relatively hydrophobic. It provides enhanced storage stability for reactive compounds (e.g., vinyl acetate, NIOSH Method 1453, and 2-butanone, NIOSH Method 2500), but is not sufficiently inert at high temperatures to be useful in thermal desorption techniques (see below) [99]. Other Carboxens can be very hydrophobic, and have specific applications [100,101].

7.5. Porous polymers

Tenax (see below for more details) is rarely used with solvent desorption, as it has low capacity for volatile compounds, and is incompatible with many solvent systems. It is used in specialized methods [102–104], e.g., for certain explosive chemicals. Amberlite XAD-2 and Chromosorb 102 are similar mesoporous polymers with moderate surface areas that are often used for large, semi-volatile molecules such as polyaromatic hydrocarbons and pesticides [105,106]. Amberlite XAD-2 is often used as a support for derivatizing agents. Porapak N [107] and certain other members of the Amberlite series (e.g., XAD-7 [108]) have polar adsorption sites suitable for polar molecules.

The most frequently encountered polymers used with solvent desorption are microporous poly-styrenes. The degree of porosity can be controlled by the amount of cross-linking, and divinylbenzene is often incorporated for this purpose. The polymers absorb no significant water and exhibit inert surfaces to reactive molecules such as terpenes. They are compatible with common desorption solvents. Chromosorb 106, Amberlite XAD-4, Porapak Q and Hayesep D are all similar in this respect. Their surface areas lie in the region of 400–800 m^2 g^{-1}, and they all have considerable capacity for volatile molecules, although not for the most volatile (e.g., dichloromethane). Chromosorb 106 is most commonly used [28,69,99,109–111], sometimes with a back-up of charcoal to collect the very volatile components. However, it is significantly more expensive than charcoal, and sorbents are not reused after solvent desorption.

7.6. Carbon molecular sieves

Molecular sieves have an abundance of micro-

pores in a size range of molecular dimensions. Molecules larger than the pores will pass straight through the bed, and hence the ''sieve'' effect. On the other hand, small molecules, which can fit snugly within the pores are held very tightly. Carbon molecular sieves have very high capacities for small, volatile molecules, such as methyl chloride, dichloromethane and vinyl chloride [33,94,100,101]. Unfortunately, water too collects in these small pores, although this does not have a great effect on the capacity as these sorbents are much less hydrophilic than coconut charcoal, since they are manufactured from polymers such as polyvinylidene chloride. The adsorbed molecules are held very tightly so that a solvent with a high heat of adsorption is required for effective displacement and recovery. Carbon disulfide is suitable, but methanol is not.

8. Thermal desorption

A 1-ppm amount of a hydrocarbon in air is equivalent to around 3 ng ml^{-1}. The sensitivity of the detectors available to GC means that only 10 ml of air need be introduced to the detector. Even though a 10-l air sample on a sample tube is diluted a 1000-fold by using liquid desorption there normally will be sufficient sample for quantitative analysis. A 10-l sample is consistent with small, personal air sampling pumps operating at 200 ml min^{-1} over an 8-h period. However, many compounds today have limit values, or at least action levels, below 1 ppm, and there may be a requirement for sampling shorter periods (e.g., 15 or 30 min). The small increase in sensitivity that can be obtained by increasing the flow-rate through the tube is generally not sufficient to obtain the 10–100-fold increase in sensitivity required for these analyses. Samples taken from relatively unpolluted environments (homes, offices, outdoors) can not normally be analyzed using solvent desorption without additional sample concentration, and a procedure involving concentration, dilution and re-concentration is unwieldy in practice and prone to errors.

Two other methods are available for concentrating the contaminants in air. The first, cryofocusing, involves freezing the components out in a trap held at temperatures close to that of liquid nitrogen. This procedure consumes expensive liquid cryogen, is

prone to blockage from water ice, and sample degradation from condensed oxygen. The second procedure involves sorbent trapping (as with solvent desorption), but sample recovery by a non-diluting process. In practice, this recovery mechanism is through the application of heat (although microwave desorbers exist they are uncommon). Thermal desorption has a long history in air sampling [4,21,24,112,113]. Thermal desorption can be used with sorbent traps that were exposed in the field, or a whole-air sample can be returned to the laboratory and the contaminants concentrated and desorbed in one procedure. Containers for whole-air samples include stainless canisters (EPA Compendium Method TO-14), typically treated internally to reduce sample losses (e.g., the SUMMA or SilicoSteel processes), or polymer bags (e.g., Tedlar or Mylar) as used in EPA SW846 Method 0040. The potential for rapid losses from polymer bags exists, so that canisters are much preferred for storage of more than a few hours. Both types of container are available in sizes ranging from a few hundred milliliters up to several liters. While these containers can be analyzed using a direct gas injection through a gas-sampling loop or syringe, the long time-period for the injection can lead to chromatographic band-broadening and loss of resolution and sensitivity. More commonly, the sample is passed through a narrow focusing tube. As in cryogenic sample collection, this could be an empty capillary tube held at very low temperature using liquid cryogen [114], although the procedure has the same drawbacks of ice blockage and oxygen condensation. An alternative method is to use a larger tube containing a fine-grained (80–120 mesh) sorbent, typically at reduced temperature (-10 to $-30°C$). This narrow tube can be heated rapidly to release the trapped contaminants as a fast, "plug" injection into the chromatograph.

When sampling using sorbent tubes, the sorbent could be thermally desorbed directly into the gas chromatograph. However, there is a significant time-factor involved in transferring all of the trapped contaminants from a large tube, and any trapped water vapor, or residual oxygen within the tube, will also be transferred. It is much better to purge oxygen and water vapor from the tube first, using dry carrier gas at ambient temperature, followed by desorption and recollection on the same kind of cooled secondary sorbent trap as described above. Rapid heat-

ing again forces the sample onto the column in a plug injection.

The acceptance of thermal desorption has suffered because the entire sample normally is consumed in a single analysis. Where the sample is used to make regulatory decisions, a second analytical result is useful. Modern thermal desorption equipment incorporates design modifications to allow re-collection of split sample on a fresh tube for archiving [115] or immediate analysis. Some sampling protocols require the collection of multiple samples. This can be done using a single pump and multiple tube-holder with independent flow controls. Another drawback to thermal desorption is that the sorbent tubes designed for this use do not possess a back-up section to detect breakthrough. While it is possible to join separate tubes together, it is rarely done in practice. The normal procedure to avoid sample loss is not to exceed "safe sample volumes" (see discussion in Section 4 above). In the absence of experimentally validated data, the use of two sample tubes operating at different flow-rates for the same time-period ("distributed sample volumes") is a suitable interim solution. The concentration results from the two samples should agree for the results to be acceptable. This approach is used in EPA Method TO-17 [116].

The tubes used to hold the sorbent for thermal desorption are made of stainless steel or precision-bore borosilicate glass, with very precise dimensions to ensure leak-free connection to the desorption apparatus. Each tube is then marked with a unique serial number, sampling direction arrow, and filled with expensive polymer sorbent. The tubes must then be thermally conditioned for several hours at around 20–30°C lower than the maximum operating temperature of the sorbent with a flow of inert gas through the tube. The tubes are then capped for storage. Leak-tight connections are required to ensure there is no ingress of ambient air. This is usually achieved with PTFE ferrules and metal screw-type fittings. Storing the tubes with a charcoal "scavenger" will help minimize the possibility of re-contamination. Care must be taken to ensure the fittings do not work loose, for example by changes in temperature or pressure. The shelf-life of a properly prepared tube may be many months, but standard protocols often call for tube re-conditioning immediately prior to use where storage has been more than
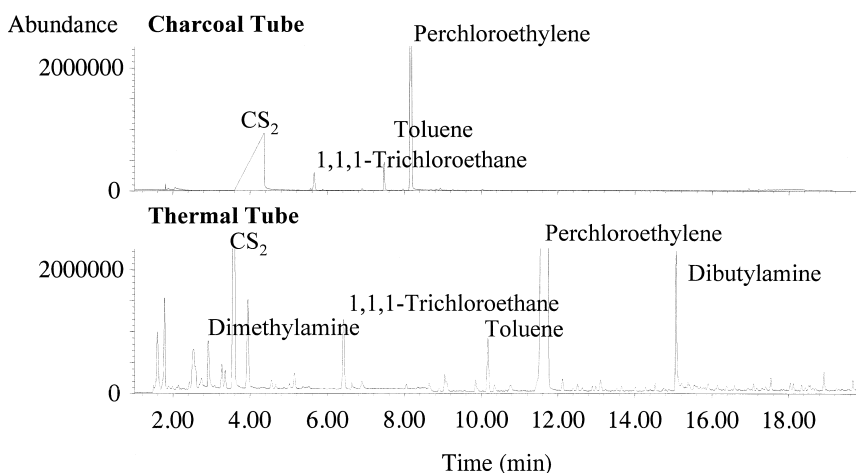
Fig. 2. Difference in sensitivity between solvent and thermal desorption. (1) Samples taken from a factory producing rubber mouldings. Solvent desorption samples were collected on 100 mg front-section charcoal tubes (note amines not detected by this procedure). Thermal desorption samples were collected on Carbotrap C–Carbotrap B–Carboxen 569 multi-bed tubes. Analysis on 30 m×0.25 mm I.D. DB-1 column (1 μm film thickness) in a Hewlett-Packard 5890 GC system with HP 5970 mass-selective detector.

30 days. Typically, the initial cost of a thermal desorption tube is around 100-times that of a charcoal tube, although it is re-usable. Quality assurance samples (blanks, standards and reference materials) also require tubes, adding to the initial expense. In addition, there is the capital outlay for the desorber itself, typically between about US$15 000 to US$40 000 depending on whether the unit is single-tube or has automated multi-tube capability.

Thermal desorption has an advantage over solvent desorption in the lesser quantities of solvents used, with consequent implications for laboratory safety and waste disposal. However, the main advantage of thermal desorption, as previously mentioned, is the enhanced sensitivity that can be achieved. In many situations, this factor alone compensates for the higher cost of the analysis. Two examples of the difference in sensitivity between thermal and solvent desorption are illustrated in Figs. 2 and 3.

9. Sorbents used in sampling with thermal desorption

The commonest sorbents used for sampling with solvent desorption, activated charcoal and silica gel, are only rarely encountered where thermal desorption is required. This is because their high surface activity

can lead to sample degradation at the high temperatures required for desorption [117]. Conversely, the sorbents most commonly used for thermal desorption, such as Tenax and Carbotrap, are rarely used with solvent desorption as their capacities are not compatible with large sample volumes at high concentrations. There is some overlap, however, for example Chromosorb 106 is commonly used for sampling moderate to high concentrations with either solvent or thermal desorption. A useful review of sorbents for thermal desorption has been published [4].

9.1. Tenax TA

Tenax TA, often referred to simply as Tenax, is a macroporous, semi-crystalline polymer manufactured from diphenyl-*p*-phenylene oxide (DPPO). It has a relatively low surface area (about 15 m^2 g^{-1}). The consequent low adsorption capacity of Tenax limits its application in atmospheres of high concentrations, since, as previously noted, breakthrough is dependent on concentration. However, its ability to be conditioned to have a very low background (less than 1 ng per component), together with its high temperature stability that allows for the recovery of many semi-volatile molecules, makes it a very useful sorbent for collecting multiple organic compounds
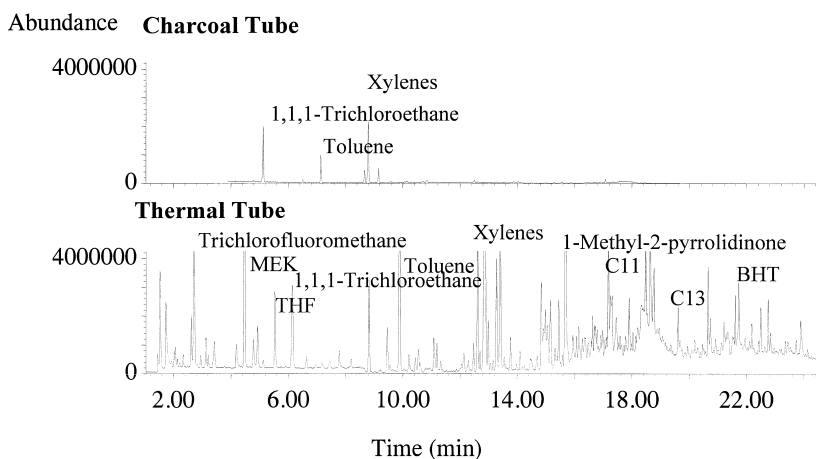
Fig. 3. Difference in sensitivity between solvent and thermal desorption. (2) Samples taken inside new truck cabs to detect off-gassing components. Solvent and thermal desorption tubes and analytical equipment as in Fig. 2.

from atmospheres of low concentrations, such as when monitoring ambient or relatively unpolluted indoor air [113,118,119]. Many methods from the US EPA and the UK HSE employ Tenax. Because of its high thermal stability Tenax can also be combined with carbonaceous sorbents in sorbent tubes containing multiple-beds (see below). Tenax has been directly combined with graphite (Tenax GR) in various proportions. However, it is debatable whether this offers any advantage over having separate beds. Tenax is attacked by oxidizing gases in the atmosphere, such as ozone, and nitrogen oxides, with the formation of artefact compounds such as acetophenone and benzaldehyde from ozone [120–123] and 2,6-diphenyl-*p*-benzoquinone from nitrogen oxides [124–126]. The same compounds may also be formed via radicals formed through the reaction of oxidants with adsorbed VOCs [126]. Reactive compounds such as unsaturated terpenes, can also be degraded through reaction with ozone [122,127,128], although this problem is not unique to Tenax [129]. Ozone scrubbers have been suggested to minimize this problem [53,121,122,128,130] although none appeared perfectly suitable [53]. Tenax is relatively hydrophobic, although the capacity for polar compounds, such as alcohols, appears to increase at high humidities suggesting some minor water uptake. Tenax is granular and available in a wide-range of mesh sizes. The relatively inert nature, high thermal stability and rapid desorption kinetics

make it a very suitable sorbent for the secondary cold-trap of thermal desorbers.

9.2. Chromosorb 106

Chromosorb 106 (see above) has a greater capacity than Tenax, and can be used at much higher concentrations. Its thermal stability is lower than that of Tenax, and so it is not suitable for semi-volatile compounds or for mixing with other sorbents. In addition, it can not be conditioned to as low a background, especially for aromatic species, and the background tends to increase with storage. It is not certain whether this represents sorbent breakdown to release monomer, or insufficient cleaning followed by migration of adsorbed molecules from depth. Nevertheless, it is not suitable for accurately sampling low ppb concentrations, although it remains one of the most popular and versatile sorbents for sampling for industrial hygiene applications [99]. It is very hydrophobic and relatively unaffected by ozone [129]. Porapak N has also been used in thermal desorption applications (e.g., Ref. [131]), as has Porapak S [132].

9.3. Graphitized carbons

The type example of these sorbents are the Carbotraps [99,101,133–135]. Carbotrap C has a low

surface area (around 10 m^2 g^{-1}), and is normally used in combination with other sorbents in multi-bed tubes (see below). Carbotrap B, known also simply as Carbotrap, has a higher surface area (around 100 m^2 g^{-1}) and is sometimes used alone, but is more commonly also found in multi-bed tubes (see below). The graphitized carbons are made from carbon black and tend to be soft and friable, which can cause problems if tiny particles are allowed to enter the thermal desorber apparatus. While relatively hydrophobic, graphitized carbons do absorb some water. Certain compounds, such as terpenes and chlorinated hydrocarbons can be unstable when adsorbed on these sorbents [136]. The disappearance of terpenes may be due to re-arrangements catalyzed by the carbon surface [128], although De Bortoli et al. [136] were able to eliminate the effect by replacing the stainless steel sorbent retaining screens with gold-plated ones. Ozone does not produce artefacts from the sorbent itself. Very recently, a high surface area version has been developed [137], which promises to have useful applications.

9.4. Carbon molecular sieves

Carbon molecular sieves are rarely used alone, except when targeting specific chemicals. They typically are used as the rear section in multi-bed tubes (see below). They are required for the collection of the most volatile organic compounds, although they will also collect water molecules. Water can be a problem in thermal desorption analyses, either because it can freeze in the cryotrap and block it, or because when rapidly heated the momentary overpressure can lead to split discrimination, or because it can alter the polarity of the carrier gas or column. A protocol using a dual polar/non-polar column has been used to minimize water interference in analysis [138]. An ambient purge of between 30 and 300 ml of dry carrier gas has been shown to remove most of the collected water without causing significant loss of analyte [139].

Many kinds of carbon molecular sieve are available (e.g., Carbosieve S-III, Carboxen 1000, Carboxen 1003, Spherocarb, Anasorb CMS [31,96,100]). Retention volume studies have indicated large differences between these sorbents. Whether this relates to a practical difference is uncertain at this time. Until comparisons are carried out it is advisable not to treat these sorbents as equivalent, and to use only the material evaluated in the specific method.

Zeolite molecular sieves are used in a few methods, for example in sampling butadiene, or nitrous oxide.

9.5. Multi-bed tubes

Tubes containing beds of different sorbents have become popular in recent years [4,31,116,140–142]. Such tubes have formed the basis of recent US Government agency methods (NIOSH 2549 and EPA TO-17). Typical combinations include Tenax TA or GR and carbon molecular sieve, and low surface area graphitized carbon/medium surface area graphitized carbon/carbon molecular sieve. Examples include the Air Toxics Tube and the Carbotrap 300 tube available from Supelco. The arrangement of the sorbents is such that the least volatile compounds are trapped on the weakest sorbent at the front end of the tube, and successively more volatile compounds are trapped by increasingly strong sorbents further down the tube, with the most volatile being trapped at the far end. The distribution of analytes on a typical tube can be determined by desorbing the beds seperately, as illustrated in Fig. 4. Desorption then takes place in the reverse direction, as with single-bed tubes. These tubes have the advantage of potentially being able to collect most volatile compounds of interest in a single sample and, with suitable gas chromatographic column and temperature program, obtain a result with a single analysis. Care must be taken to ensure that chemicals do not break through to be adsorbed on strong sorbents from which they cannot be recovered immediately. One method to test this is to examine the standard deviation in results of analyses of a standard atmosphere using different sample volumes. In one study 12% of VOCs tested on one multi-sorbent combination and 13% of VOCs tested on another failed to meet 20% relative standard deviation criteria with three different sample volumes [141]. However, most of these failures involved the same highly volatile VOCs that had greater than 5% breakthrough through the entire tube. Storage stability experiments are also required to ensure sample breakdown or migration does not occur, and some laboratory studies have already been
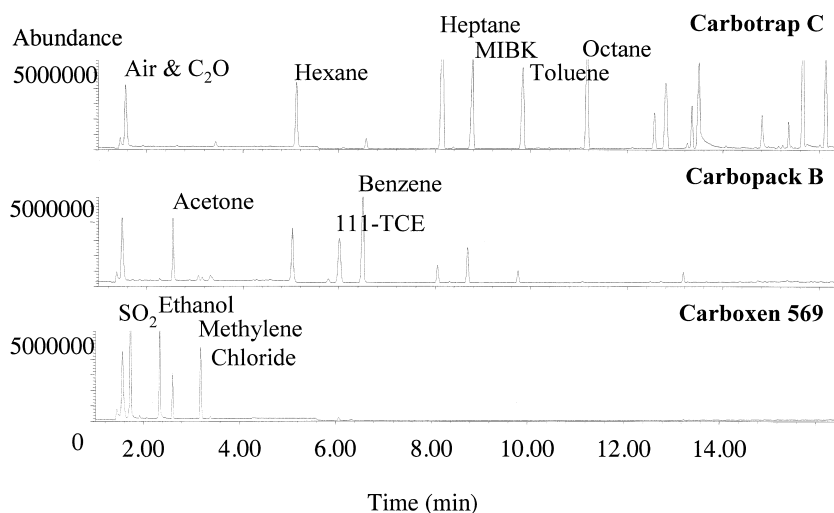
Fig. 4. Illustration of the segregation of sampled components on a multi-sorbent bed tube. Each section analyzed separately. Analytical equipment as in Fig. 2.

carried out [140,142] using selected sorbents and combinations of sorbents. In general, storage is acceptable for most compounds. Of the compounds that were tested in one study [142], 1,1,2,2-tetrachloroethane, bromomethane and styrene were the most troublesome for all sorbent types and combinations, although there were some other VOCs not stable on all sorbents and combinations. In another study using different combinations of sorbents and a much larger compound list, most compounds exhibited recovery of 95% or better after 8 days, and about 80% exhibited recovery of 90% or better after 27 days. Poor results were obtained with chloroethene, bromomethane and ethyl acrylate (and not with 1,1,2,2-tetrachloroethane or styrene). The first study used 70–700 ng per component, the second study used less than 30 ng per component. A further study using the principle of distributed sample volume pairs has been carried out [116]. In this study samples were taken at two different flow-rates to cover the same time-period. The sample volumes were 4 l and 1 l, respectively. Most compounds met the requirement of 75–125% agreement between the concentrations measured from the two different sample volumes, especially at low humidity. The most volatile chemicals, especially freons, were most apt to fail. At high humidity, the quantity of compounds collected in the 4-l sample were less than

four-times the quantities collected in the 1-l sample indicating sample loss by breakthrough. A second group of less volatile compounds also had ratios lower than 4:1 at high humidity, and this was interpreted as possible breakthrough from a weaker to a stronger sorbent bed within the tube.

All of these studies have indicated significant breakthrough of very volatile compounds even using small sample volumes (5 l or less) and low concentrations (10 ppb or less). Because of the relationship between breakthrough and sample volume and concentration, caution is required when using these sorbent tubes for industrial hygiene purposes where sample volumes collected over a work-shift are typically larger (10 l or more) and the likely concentrations may be higher by a factor of 10 000. At such high concentrations, it is possible to analyze smaller sample volumes, but it is not possible to run sampling pumps much below 20 ml min^{-1} (equivalent to a 10-l sample over 8 h) without interference from diffusive processes. It is possible to use diffusive samplers with lower uptake rates (see below).

10. Sorbents for sampling inorganic gases and vapors

Most of the previous discussion concerned the

collection of organic gases and vapors. Some inorganic gases and vapors are also important, particularly in occupational hygiene [143]. A mixed copper/manganese oxide (Hydrar or Hopcalite) is used for collecting mercury vapor. High-purity silica gel is commonly used for collecting acid gases (e.g., HCl, H_2SO_4). Acid-coated sorbents (e.g., silica gel, charcoal, firebrick) are used for basic gases such as ammonia, phosphine and hydrazine. Alkali-treated charcoal is used for collecting sulfur dioxide. Triethanolamine coated on an inert sorbent is commonly used for nitrogen oxides and sulfur dioxide. In ambient monitoring methods real-time techniques are available for most of these applications. However, sorbent-based diffusive sampling methods (see below) are popular as a cheap method for obtaining widespread spatial coverage. Such methods exist for ozone [144–146], nitrogen oxides [147,148], sulfur dioxide [148,149], ammonia [149,150], and carbon monoxide [151], amongst others.

11. Sorbents for diffusive sampling

Diffusive samplers (sometimes called diffusive monitors, passive samplers or passive monitors [152]) are used in a method of sorbent sampling without the need for an air mover (pump).

Diffusive sampling [153–157] operates by allowing gas or vapor molecules to diffuse through a defined volume of still air (or, less often, through a polymer membrane) until they reach a sorbent bed. This movement is controlled by Fick's first law, in which the rate of diffusion is a function of the concentration difference between the two ends of the diffusion path and the geometry of the path. Given a fixed geometry, and a zero concentration at the sorbent bed due to adsorption or reaction, the mass collected is a function of the external concentration and the diffusion coefficient of the molecules. The diffusion coefficient varies in a known manner with temperature and pressure, and the result can be corrected for these parameters.

Typically, the same sorbents are used in diffusive samplers as in pumped sorbent tubes, and again, the selection normally depends on the method of recovery (solvent or thermal desorption) and the method of analysis (GC, HPLC, etc.). However, the sorbents used with thermal desorption have additional considerations when used with diffusive sampling [158]. The uptake rate of a diffusive sampler is related to the concentration at the sorbent surface. Provided all the molecules arriving at the surface are adsorbed the uptake rate will be constant. Where the sorbent is "weak", and a significant vapor pressure of the adsorbed molecules exists above the sorbent surface, one of several scenarios is possible. In the first, the rate at which molecules arrive at the sorbent surface is slowed due the change in diffusion gradient, and the uptake rate falls [159]. If adsorbed molecules that leave their adsorption sites are free to migrate deeper into the sorbent bed, the uptake rate will not decrease to zero, but will fall as the effective diffusion path-length increases [160]. Finally, if the concentration external to the sampler falls molecules in the vapor phase above the sorbent may diffuse out of the tube along the new gradient [161] (this is one type of the phenomena known collectively as reverse diffusion). All of this non-ideal behavior causes the uptake rate to fall with time. Theoretical and empirical models have been established to account for this [162,163]. However, these effects are modified by ambient conditions (e.g., temperature), and it is important for such techniques to be properly validated before the results can be considered quantitative. Several protocols are available for testing samplers for occupational hygiene applications (HSL, ASTM, ANSI, CEN) and some diffusive sampling methods have been validated by government agencies such as OSHA (charcoal sorbent and solvent desorption) and the HSL (polymer sorbent and thermal desorption), and these methods may be found in their respective methods manuals. The Comité Européen de Normalisation is currently developing a test protocol for the proper validation of long-term diffusive sampling methods, and it is important to standardize such a protocol since several diffusive sampling methods are now used regularly for ambient air monitoring of VOCs [164,165], and not all these methods have been rigorously tested. In particular, the change in uptake rate with time of diffusive samplers containing polymer sorbents requires careful study [158,166]. Dual sorbent bed tubes also have been suggested as diffusive

samplers [167], but they are not commonly used at present.

12. Disadvantages of sorbent sampling

The principal disadvantage of sorbent sampling is that it is not a real-time technique. It is possible to sample ambient air over a long period by taking short-term samples (e.g., 5 min) out of every hour [168], and automated equipment is now available in which one tube is being analyzed while another is collecting sample [169] to ensure complete temporal coverage. However, this is still not the near real-time results that are possible with some techniques, such as Fourier transform infrared spectroscopy (FT-IR). For monitoring certain species, such as chemical warfare agents, where near-real time alarms are a necessity, ultra-short columns and rapid chromatography can give results in around 2 min. Another disadvantage is the limitations on the range of compounds that can be collected. More than one sorbent is required to cover all classes of compound (for example three different sorbents would normally be required to sample amines, aldehydes and aromatic hydrocarbons). Certain compounds simply do not show good stability on sorbents, despite much research to find a suitable substrate. A particularly good example is the reduced sulfur gases (H_2S, CS_2, mercaptans). Three separate NIOSH sorbent-trapping methods would be required to sample these compounds, and none are considered ideal methods. Another set of compounds which present difficulty in sorbent collection are the very volatile hydrocarbons, such as methane, ethane, ethylene and propylene. All of these compounds are amenable to whole-air sampling using containers. This is a method that has undergone much evaluation by the US EPA [170,171] and shows great promise for industrial hygiene now that suitably small, inert containers are available. Ozone is considered less of a problem in canister sampling due to its rapid disappearance through autoxidation reactions. Finally, containers can be fitted with orifices that allow either an almost instantaneous fill, or the collection of a time-weighted average sample. However, flexibility is limited as a wide variety of canister sizes and orifice flow-rates would be needed to cover the same range of sample times and volumes available with a single flow-rate adjustable pump and sorbent tube.

13. Quality assurance

For best results it is important to use validated methods within the limitations of the variables covered by the validation protocol. Alternative methods can be validated in the field against existing reference methods. Pumps should be properly calibrated or diffusive uptake rates should be experimentally verified. Pressure and temperature corrections should be made where necessary.

Sorbent tubes should be properly labeled and sealed. Proper sealing is essential when monitoring very low concentrations, as contamination can easily enter through poor end-fittings. Blank sorbent tubes, opened and immediately re-sealed in the field, can be used to measure contamination during transport or storage. Unopened sorbent tubes from the same lot or batch are used to determine blank sorbent backgrounds. Back-up sections or distributed volume sets can be used to detect breakthrough [116,172]. Dual sampling trains where one of the trains is pre-spiked with the analyte of interest can also be used to ensure proper sample collection and recovery (e.g., 40 CFR 60 Appendix A Method 18). Instrument calibration is through liquid standards (solvent desorption) or spiked sorbent tubes (thermal desorption). Reference standards for thermal desorption are now available on pre-spiked tubes [173–175]. Proficiency test samples for both solvent and thermal desorption analyses are available in many countries, for example through the American Industrial Hygiene Association or the Workplace Analysis Scheme for Proficiency (Health & Safety Lab., Sheffield, UK). Tubes containing sorbents that are used with solvent desorption are single-use, but thermal desorption tubes are frequently re-used. This can lead to carryover of poorly desorbed compounds which then appear in later analyses, and it is best that the tubes are individually numbered and referenced to an analytical log so that any such problems can be traced to their origin. There is very little published work on the ability of sorbents to be re-used. In

addition to the problem of carry over, sorbents can degrade both mechanically and chemically. Rothweiler et al. [128] noted changes in Tenax TA after five uses, but not Carbotrap after 30 uses, while De Bortoli et al. [136] noted no change in Tenax TA after 38 uses, nor Carbotrap after hundreds. Rothweiler et al. used liquid, rather than vapor spikes, which may account for the difference.

14. Solid-phase microextraction

Solid-phase microextraction (SPME) is a novel technique in which sampling and pre-concentration of analytes are combined into a single step, and then the analytes are directly transferred into a standard gas chromatograph [176]. Adsorption takes place on a small length of fine fiber projecting from the needle of a syringe. The fiber is protected during storage and transport by retracting it into the syringe needle or barrel, and capping the end of the syringe. The fiber possesses a coating of a sorbent material. Both typical gas chromatographic liquid phases (polydimethylsiloxane) and adsorbent carbons (Carboxen, Carbotrap) have been evaluated for collecting general organic vapors, with the poly(dimethylsiloxane) coating exhibiting the best recoveries. Reactive chemicals can be added to the coating which enable specific analytes such as formaldehyde [177] or amines [178] to form derivatives. In all cases, analysis is simply by piercing the gas chromatograph inlet septum with the syringe needle and ''injecting'' the fiber into the heated zone of the injector port, where the collected analytes are desorbed thermally directly into the carrier gas stream. Optimum separations are achieved by cryogenic focusing within the GC oven. However, this is expensive and not available in portable chromatographs; reasonable separations are possible without it. A method has been published for estimating air concentrations of complex hydrocarbon mixtures without the need for individual component calibration, and consequently establishing a value for total petroleum hydrocarbons in air [179].

Advantages of SPME include:
1. Sampling device is lightweight and compact.
2. Reagents are not required for desorption.
3. Sensitivity is good.
4. Response is linear with concentration.
5. Generally independent of humidity (except at very high humidities)
6. Expensive cryotraps or thermal desorbers are not required.

Drawbacks of SPME include:
1. Analytes of low volatility do not reach partition equilibrium quickly. (Non-equilibrium theory has been developed [180]).
2. Equilibrium composition varies widely with temperature. (Corrections for temperature have been developed [181]).
3. Storage stability is poor (less than 1 h except under refrigeration).
4. Samples are not time-integrated.
5. Gas standards are required for calibration [182].
6. Whole sample is used.

Until the effects of environmental variables on sampling and recovery are better known, the best use of SPME appears to be in the analysis of canister samples or the head-space analysis of solvent-extracted sorbent samples [183].

15. Conclusion

Sorbents are commonly used in the following areas of sampling: (1) where information is required concerning the spatial distribution of chemicals in the atmosphere; (2) where personal samples are required; (3) where complex mixtures of organic compounds are best resolved by laboratory analysis and (4) where long-term measurements are required.

In environmental monitoring there is some overlap between canister sampling and sorbent sampling, although sorbents are often used in the pre-concentration of canister samples prior to analysis, for example in the secondary traps of thermal desorbers, or with SPME analysis of canister samples. In general, canisters are more useful for very volatile (C_1 and C_2 hydrocarbons) and reactive compounds (e.g., 1,3-butadiene), while sorbent tubes are more useful for less volatile and polar compounds, although there is a wide middle ground where both could be applicable. It is also possible for sorbent tubes to be used for semi-volatile compounds, even with thermal desorption [184]. In occupational hygiene investigations sorbent sampling has been the

norm since the 1960s, as small, lightweight and inert canisters with well-defined sampling orifices have only recently become available. It will be interesting to see what further developments may occur in this field. While solvent desorption remains the recovery procedure of choice in occupational hygiene analyses at the present time, thermal desorption is gaining ground. An illustration of the utility of thermal desorption when sampling trace odor constituents in a candy factory is given in Fig. 5. Sorbent sampling has many exciting new applications, including sampling of exhaled breath [185–187].

Research continues in the area of sorbents, sometimes involving novel adsorbents such as polymers [188], clay minerals [189], or even crab shells [190]. In addition, the database of existing sorbent properties and behavior continues to expand, leading to better selection of the most appropriate materials, especially with regard to developments in analytical chemistry. Further work is required in the theoretical area of sorbent sampling. Unfortunately, knowledge and experience are not always passed on to the field researcher, and it is important to stress the need for communication between the analytical laboratory and field personnel when selecting air sampling methods. Until the analytical laboratory has been fully miniaturized (e.g., the ''GC-on-a-chip''), there will continue to be a need for sorbent sampling, although, in the future, sorbent sampling should ultimately be replaced by monitors that can give specific and sensitive, instantaneous and time-weighted average results, without the need for waiting on laboratory analysis.

Appendix A. Standards

Workplace Atmospheres – General Requirements for the Performance of Procedures for the Measurement of Chemical Agents (EN 482: 1994).

Workplace Atmospheres – Requirements and Test Methods for Diffusive Samplers for the Determination of Gases and Vapours (EN 838: 1995).

Workplace atmospheres – Requirements and test methods for pumped sorbent tubes for the determination of gases and vapours (EN 1076: 1997).

Workplace Atmospheres – Requirements and Test Methods for Short Term Detector Tube Systems (EN 1231: 1996).

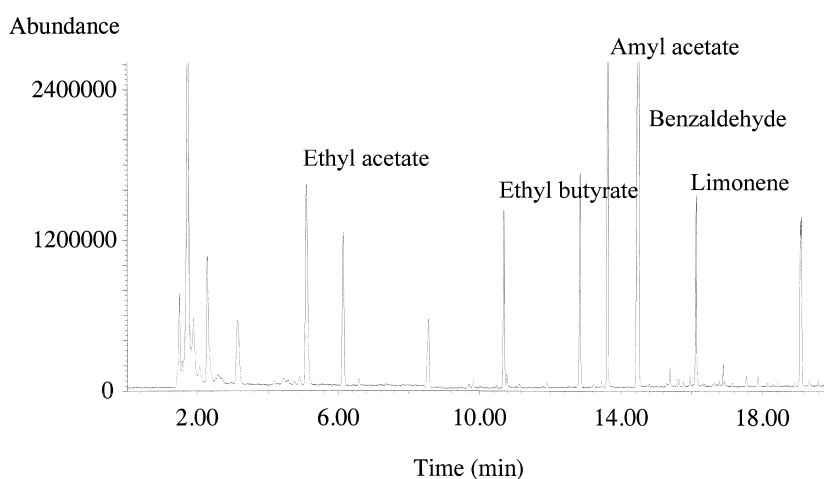Workplace Atmospheres – Requirements and Test

Fig. 5. Analysis of workplace air: trace odor components in a candy factory manufacturing chocolate-covered cherries. Thermal tubes and analytical equipment as in Fig. 2.

Methods for Pumps for Personal Sampling of Chemical Agents (EN 1232: 1997).

ISO 8762:1988 Workplace Air – Determination of Vinyl Chloride – Charcoal Tube/Gas Chromatographic Method.

ISO 9486:1991 Workplace Air – Determination of Vaporous Aromatic Hydrocarbons – Charcoal Tube/Solvent Desorption/Gas Chromatographic Method.

ISO 9487:1991 Workplace Air – Determination of Vaporous Chlorinated Hydrocarbons – Charcoal Tube/Solvent Desorption/Gas Chromatographic Method.

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