



Health and Safety Executive  
Occupational Medicine and  
Hygiene Laboratory

## MDHS 70

Methods for the  
Determination of  
Hazardous Substances

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# General methods for sampling airborne gases and vapours

### INTRODUCTION

1 This publication deals with the collection and analysis of gases and vapours commonly found in the workplace environment. It is limited to descriptions of sampling methods for subsequent laboratory analysis. It does not, therefore, include any discussions of direct reading instruments, colorimetric indicators, tape samplers, and other 'on the spot' testing devices.

### Requirements of the COSHH Regulations

2 The Control of Substances Hazardous to Health (COSHH) Regulations require that persons who may be exposed to substances hazardous to health receive suitable and sufficient information, instruction and training. The COSHH Regulations also include a requirement to assess the health risk created by work involving substances hazardous to health, and to prevent or control exposure to such substances. Employers must therefore ensure that the requirements of the COSHH Regulations are fully satisfied before allowing employees to undertake any procedure described in this method.

### NATURE OF INDUSTRIAL GASES AND VAPOURS

3 While it is true that at ordinary temperature and pressure, gases and vapours will both diffuse rapidly and form true solutions in air, they differ in other respects. Gases are generally understood to be non-condensable at room temperature and under ordinary conditions exist in the gaseous state even when present at high concentrations. Vapours are derived from volatile liquids and may condense at high concentrations, and an aerosol (particulate) form may coexist with vapour. However, unless an aerosol is produced as in a spray operation, or as 'fly', atmospheric concentrations of vapour pollutants rarely reach saturation conditions, except in enclosed spaces. With these exceptions, gases and vapours can be considered similar, and the same devices used to collect them.

### SAMPLING PROCEDURES

4 There are two basic methods for collecting gaseous samples. In one, called grab sampling, an actual sample of air is taken in a flask, bottle, bag or other suitable container; in the other, called continuous

or integrated sampling, gases or vapours are removed from the air over a measured time-period and concentrated by passage through a solid or liquid sorbent.

5 The first method involves the collection of samples over a period of a few seconds up to a minute or two. This type of sampling is used when peak concentrations are sought or when concentrations are relatively constant. The availability of modern laboratory instruments means that this technique can have high sensitivity, limited only by the detection limit of the analytical methods used. Vinyl chloride, for example, is measurable in grab samples by gas chromatography at levels well below 1.0 ppm. The collection efficiency of grab sampling is normally 100%. On the other hand, sample decay can occur from sorption or other losses, and grab sampling must be used with this clearly in mind.

6 Grab sampling is of questionable value if: a) the contaminant or contaminant concentration varies with time, or b) when the concentration of atmospheric contaminants is low, or c) a time weighted average exposure is desired. In such circumstances, integrated sampling is used instead.

7 During integrated sampling, the gas or vapour is collected from air by a) solution in a liquid, b) reaction with a solution (or reagent therein), or c) collection onto a solid sorbent. Integrated sampling may be achieved either actively, ie with a sampling pump, or diffusively. The collection/recovery efficiency of both active and diffusive sampling devices may be less than 100%. After collection, however, most samples are stable, at least for a few days or weeks.

### Selection of sampling devices

8 The first step in the selection of a sampling device and analytical procedure is to search the available literature. Primary sources are the specific methods in the MDHS series<sup>1</sup> or the compendia of methods recommended by the US Regulatory Authorities, ie the *NIOSH Manual of Analytical Methods*<sup>2</sup> and the *OSHA Analytical Methods Manual*.<sup>3</sup> Recommended methods from other countries, such as Germany<sup>4</sup> or Sweden,<sup>5</sup> might also be consulted. Secondary sources are published literature references in, for example, *Annals of Occupational Hygiene*, the *American Industrial*

*Hygiene Journal, Applied Industrial Hygiene, or Analytical Chemistry* or books such as the Intersociety Committee *Methods for Air Sampling and Analysis*.<sup>6</sup>

9 If a published procedure is not available, one can be devised from theoretical considerations. However, its suitability must be established experimentally before application. Important criteria for selecting sampling devices are solubility, volatility and reactivity of the contaminant, the sensitivity of the analytical method and the availability of the proposed device.

10 Generally speaking, non-reactive and non-sorbing gaseous substances may be collected as grab samples. Water soluble gases and vapours, and those that react rapidly with reagent solutions, can be collected in simple gas washing bottles. Volatile and less soluble gaseous substances and those that react slowly with a reagent require a longer liquid contact time. For such substances, more elaborate sampling devices may be required such as gas washing bottles of the spiral type or fritted bubblers. Insoluble and non-reactive gases and vapours are collected by sorption onto activated charcoal, silica gel, or other suitable sorbent. Frequently, for a given contaminant, there may be a choice of sampling equipment.

## GRAB SAMPLERS

### Evacuated flasks

11 Figure 1 illustrates a separatory flask fitted with glass stoppered cocks on each end. These are suitable for partial evacuation, and also for displacement sampling (see below). Evacuation is achieved by drawing a vacuum through one stem while the other is kept closed, then closing the open stem before the vacuum is turned off. Similar containers are also available in plastic and metal, and are to be preferred to glass containers as there is a potential safety hazard with the latter.

12 Except for the heavy walled containers illustrated by Figure 1, no attempt is made to reduce the pressure

to zero. However, the degree of evacuation must be known and is determined from the manometer pressure or vacuum gauge. This information, along with the barometric pressure and temperature at the sampling site, is used to calculate the actual volume of air or gas collected.

### Gas or liquid displacement containers

13 Any ordinary sealable container can be used as a displacement sampler. Figure 1 illustrates one such sampler. Original air is replaced by test air by pumping or aspirating through the container with a double acting rubber bulb aspirator or a battery or electrically operated vacuum pump. The volume of air swept out should be 10-15 times the container volume to achieve a sample collection efficiency of more than 99%. This is mathematically expressed by:

$$N = 2.303 \log 100/E \quad (1)$$

where

N = number of bottle volumes swept out  
E = % error in sample collection efficiency.

14 An alternative method for sampling with these containers is to fill them with water and allow the water to drain out slowly in the test area. The liquid becomes replaced by test air. Obviously, this procedure is not suitable for collecting water-soluble gases.

15 For soluble and reactive gases, a liquid sorbent or reagent solution may be introduced into the gas displacement sampler. The usual procedure is to fill the sampler with test air and then add the sorbent. When dealing with partially or totally evacuated flasks, the sorbent is added before they are put under vacuum. In both cases, after the sample has been taken, the container is rotated to ensure an even distribution of the reagent on the inside surface of the sampler. This may take a few minutes or overnight and so the equilibration

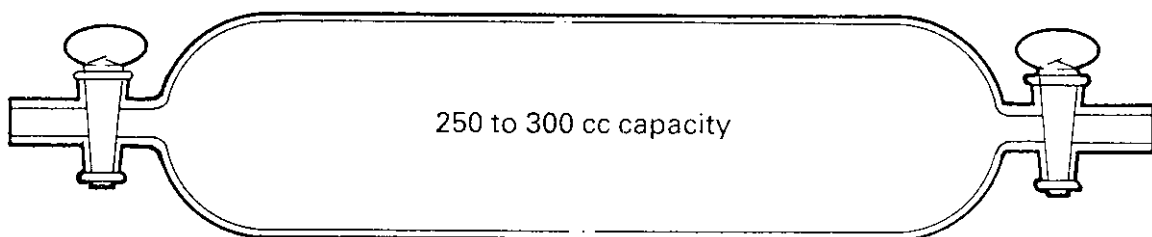


Fig 1

time must be determined experimentally.

### Flexible plastic containers

16 Plastic bags can also be used as grab samplers (and also for integrated sampling - paragraph 29). Bags are commercially available in sizes up to 250 litres, but 5 to 15 litre bags are more typically used. These bags are constructed from a number of plastic materials including polyester, polyvinylidene chloride, Teflon, or other fluorocarbons. Plastic bags have the advantages of being light, non-breakable, and simple to use. But they should be used with caution since storage stabilities for gases, memory effects from previous samples, permeability, precision and accuracy of sampling systems vary considerably.

17 Plastic bags should be tested before they are used. Some general recommendations are available in the published literature for the use of such bags for air sampling.<sup>6,9-11</sup> A good review of specific applications up to 1967 is Schuette.<sup>12</sup> Other specific applications are listed in Table 1. Posner<sup>19</sup> is a useful systematic study of five bag types and six organic vapours, and concluded that Tedlar bags are best for short-term sampling, while aluminised bags are better for long-term storage prior to analysis. Storage properties, decay curves, and other factors, however, may vary considerably from those reported for a given gas or vapour since sampling conditions are rarely identical. Each bag, therefore, should be evaluated for the specific gas or gas mixture for which it will be used. In addition, all bags should be leak tested, flushed with clean air and conditioned before use. Three pump and cleaning cycles should be enough. The conditioning is first performed for several hours in the laboratory using test atmospheres, and is repeated

**Table 1** Some storage properties of gases and vapours in plastic bags

<i>Gas or vapour</i>	<i>Bag type</i>	<i>Reference</i>
Various	Various	12
Vinyl Chloride	Aluminised	13
Hydrocarbons	PVF	14
Vinyl Chloride	Tedlar	15
Hydrocarbons	Saranex, wine mylar, tedlar	16
Benzene	Tedlar	17
Chlorinated hydrocarbons	Tedlar	18
Methanol, acetone; benzene, butadiene; butene, trichloroethylene	Saran, teflon, halar, tedlar, aluminised	19

in the field before use by filling and emptying a bag several times at the sampling site.

### Hypodermic syringes

18 Syringes of 10 to 50 ml volume have been found satisfactory for air sampling.<sup>20,21</sup> They are available in glass and disposable plastic. Gas and vapour storage and decay curves for these devices must be determined. Advantages are their low cost, convenience, and ease of use.

### ACTIVE SAMPLERS

#### Liquid sorbents

19 Four basic types of sampler using liquid sorbents for the collection of gases and vapours are: simple gas washing bottles, spiral and helical sorbers, fritted bubblers, and glass-bead columns. The sampling and sorbent capacity of these types are given in Table 2. The function of the different types is to provide an appropriate level of contact between the contaminant in the air and the liquid sorbent.

20 Petri, Dreschel, and midget impingers are

**Table 2** Sampling rate and sorbent capacity of liquid sorbent devices<sup>6</sup>

<i>Type of absorber</i>	<i>Absorbent capacity (ml)</i>	<i>Sample rate (ml/min)</i>
Simple gas washing bottle	5-100	5-3000
Spiral and helical	10-100	40-500
Fritted bubblers	1-100	500-100 000
Glass-bead columns	5-50	500-2000

examples of simple gas washing bottles. They function by applying a suction to an outlet tube which causes sample air to be drawn through an inlet tube into the lower portion of the liquids contained in these samplers. They are suitable for collecting non-reactive gases and vapours that are highly soluble in the liquid sorbent. The collection of methanol and butanol in water, esters in alcohol, and organic chlorides in butyl alcohol are examples. They are also used for collecting gases and vapours that react rapidly with a reagent in the sampling medium. High collection efficiency is achieved for example when toluene diisocyanate is hydrolyzed to toluene diamine in Marcali solution.<sup>24</sup> Hydrogen sulfide reaction with cadmium sulfate, and ammonia neutralised by dilute sulfuric acid are other examples.

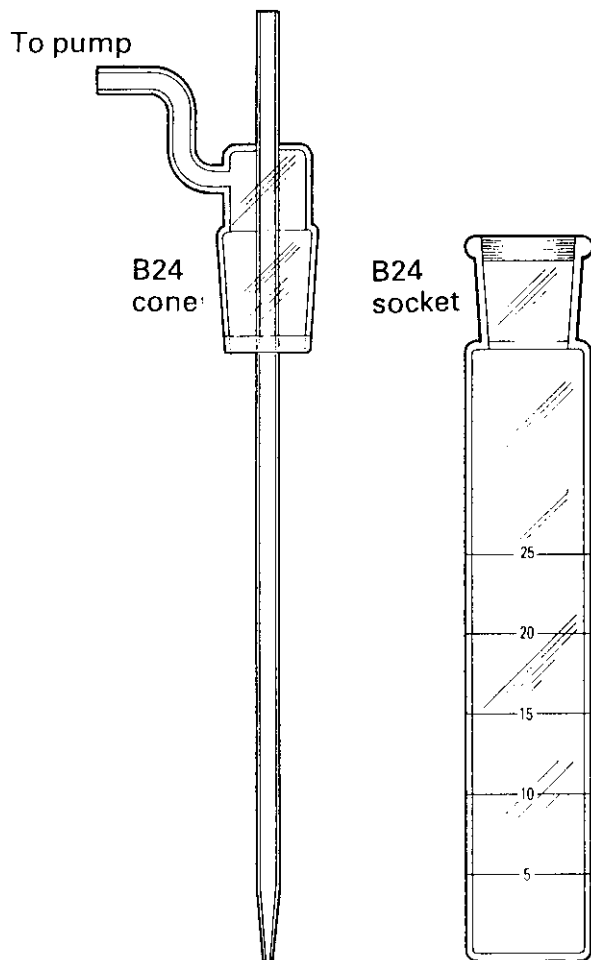


Fig 2

21 The midget impinger is the most widely used in this group and is illustrated in Figure 2. It is designed for impacting particles at a flow rate of 2.8 l/min, but for industrial hygiene use as a bubbler, it is generally used with about 10ml (but not more than 20ml) of liquid sorbent and at a flow rate of 1.0 l/min. Air sampling is performed by connecting a personal pump or other source of suction to the outlet tube. The impinger is either hand held or attached to the worker's clothing. Care must be taken that the impinger does not tilt and cause a loss of solvent or reagent, or damage to equipment. Too much liquid or an excessive flow rate will also lead to loss of sample. Spill-proof impingers have been designed to minimise this problem and are commercially available. The use of volatile impinger solvents may result in a significant toxic or flammable hazard even if spillage is avoided.

22 Friedrichs and Milligan gas washing bottles are examples of spiral and helical sorbers. They may be used for collecting gaseous substances that are only moderately soluble in or are slow in reacting with reagents in the collection media. The spiral or helical structures provide for higher collection efficiency by allowing longer residence time of the contaminant within the reagent. Such devices are appropriate for slower acting and less soluble substances.

23 Gases and vapours that are less soluble in the

collecting medium may be sampled in fritted bubblers. These are similar to the impinger shown in Figure 2, but they contain sintered or fritted glass or multi-perforated plates at the bottom of the inlet tube. Air drawn into these devices is broken up into very small bubbles and the heavy froth that develops increases the contact of gas and liquid. On the other hand, the sinter or frit can easily get blocked, and even when clear may cause a high back-pressure incompatible with some sampling pumps.

24 Packed glass-bead columns are used for special situations where a concentrated solution is needed. Glass pearl beads are wetted with the liquid sorbent and provide a large surface area for the collection of a sample. The method is especially useful when the liquid sorbent is very viscous. The rate of sampling is necessarily low; 0.25 to 0.5 l/min.

25 The efficiency of vapour collection by pure solution in liquid sorbents<sup>22, 23</sup> depends on: a) the volume of air sampled, b) the volume of the sorbing liquid, and c) the volatility of the contaminant being collected. Efficiency of collection, therefore, can be increased by cooling the sampling solution (reducing the volatility of the contaminant, or increasing its solubility), increasing the solution volume by adding two or more bubblers in series, or altering the design of the sampling device. The collection efficiency of bubblers is largely independent of the sampling rate or concentration of the vapour in air.

26 Sorption of gases and vapours by chemical reaction depends on the size of the air bubbles produced in the bubbler, the reaction rate, and a sufficient excess of reagent solution. If the reaction is rapid and a sufficient excess of reagent is maintained in the liquid, complete retention of the contaminant is achieved regardless of the volume of air sampled. If the reaction is slow and the reaction rate is not sufficient, collection efficiency will fall.

27 Several methods for testing the efficiency of a liquid sorbent device are available: a) by series testing where enough samplers are arranged in series so that the last sampler does not recover any of the test gas or vapour; b) by sampling from a gas tight chamber or tank containing a known gas or vapour concentration; c) by a dynamic standard atmosphere or from comparing results obtained with a device known to be accurate; and d) by introducing a known amount of gas into a sampling train containing the device being tested.

### Cold traps

28 Cold traps are used for collecting materials in liquid or solid form primarily for qualitative analysis. Vapour is separated from air by passing it through a coil immersed in a cooling system, eg dry ice and acetone, liquid air, or liquid nitrogen. These devices are employed when it is difficult to collect samples efficiently by other techniques. Water is extracted along with organic

materials and multi-phase systems may result.

### Plastic sampling bags

29 Plastic bags (as used for grab sampling) can also be used for collecting integrated air samples.<sup>24</sup> Samples can be collected for 8 hours, at specific times during the day, or over a period of several days. The bags may be mounted on workers as personal samplers or may be located in designated areas unattended.

### Solid sorbents

#### Charcoal

30 Activated charcoal is an excellent sorbent for most organic vapours. The relative ease with which organic vapours can be extracted from activated charcoal by carbon disulfide and be analysed subsequently by gas

chromatography are reasons for its current popularity. Today, air sampling procedures using activated charcoal are widely used<sup>30-33</sup> and form the basis of many of the official analytical methods for organic materials recommended by HSE and NIOSH.<sup>1,2</sup>

31 Analytical information on selected HSE procedures is given in Table 3. Many of these procedures are based on the extensive evaluation of the charcoal tube method by NIOSH.<sup>34</sup> This study showed that the charcoal tube method is generally adequate for hydrocarbons, chlorinated hydrocarbons, esters, ethers, alcohols and glycol ethers that are commonly used as industrial solvents. Compounds with low vapour pressure, and reactive compounds such as amines, phenols, nitrocompounds, aldehydes and anhydrides generally have low desorption efficiencies from charcoal and require alternative sorbents such as silica gel, porous polymers or reagent systems for collection.

32 Inorganic compounds such as ammonia, ozone,

**Table 3** Sorption on charcoal<sup>1</sup>

<i>Gas or vapour</i>	<i>Sample volume (l)</i>	<i>Useful range (ppm)</i>	<i>Desorption</i>	<i>Ref. (MDHS no)</i>
Acrylonitrile	20	1- 50	Carbon disulfide	1
Benzene	12	0.1- 30	Carbon disulfide	17
2-Butoxyethanol	10	0.2- 200	5% methanol in dichloromethane	21
2-Butoxyethyl acetate	10	0.2- 200	5% methanol in dichloromethane	21
Carbon tetrachloride	10	0.2- 200	Carbon disulfide	28
Chlorobenzene	10	0.2- 200	Carbon disulfide	28
Chloroform	10	0.2- 200	Carbon disulfide	28
1,2-Dichlorobenzene	10	0.2- 200	Carbon disulfide	28
1,1-Dichloroethane	10	0.2- 200	Carbon disulfide	28
1,2-Dichloroethane	10	0.2- 200	Carbon disulfide	28
1,1-Dichloroethylene	10	0.2- 200	Carbon disulfide	28
1,2-Dichloroethylene	10*	0.2- 200	Carbon disulfide	28
Dichloromethane	10*	0.2- 200	Carbon disulfide	28
1,2-Dichloropropane	10*	0.2- 200	15% acetone in cyclohexane	28
2-Ethoxyethanol	10	0.2- 200	5% methanol in dichloromethane	21
2-Ethoxyethyl acetate	10	0.2- 200	5% methanol in dichloromethane	21
Ethylene oxide	5†	0.5- 100	Carbon disulfide	26
2-Methoxyethanol	10	0.2- 200	5% methanol in dichloromethane	21
2-Methoxyethyl acetate	10	0.2- 200	5% methanol in dichloromethane	21
Styrene	10	0.1- 200	Carbon disulfide	17
1,1,2,2-Tetrachloroethane	10	0.2- 200	Carbon disulfide	28
Tetrachloroethylene	10	0.2- 200	Carbon disulfide	28
1,1,1-Trichloroethane	10	0.2- 200	Carbon disulfide	28
1,1,2-Trichloroethane	10	0.2- 200	Carbon disulfide	28
Trichloroethylene	10	0.2- 200	Carbon disulfide	28
Vinyl chloride	30‡	0.03-10	Carbon disulfide	24

\* 400 mg tube

† 700 mg tube

‡ 800 mg tube

nitrogen dioxide, chlorine, hydrogen sulfide and sulfur dioxide react chemically with activated charcoal and cannot be collected for analysis by this method.

33 Even for substances recommended for sampling on charcoal, this sorbent may not always be ideal, because of difficulty with recovery. Reference to Table 3 will indicate that for non-polar compounds, carbon disulfide is recommended as desorption solvent, while for more polar compounds, a variety of desorption cocktails is required. Difficulties arise, therefore, when sampling mixtures of polar and non-polar compounds, as each will give poor recoveries with the other's desorption solvent. Several alternative, more universal, solvents have been investigated,<sup>35-37</sup> but none of these has achieved wide recognition. In such circumstances, it may be necessary to take two samples and desorb twice.

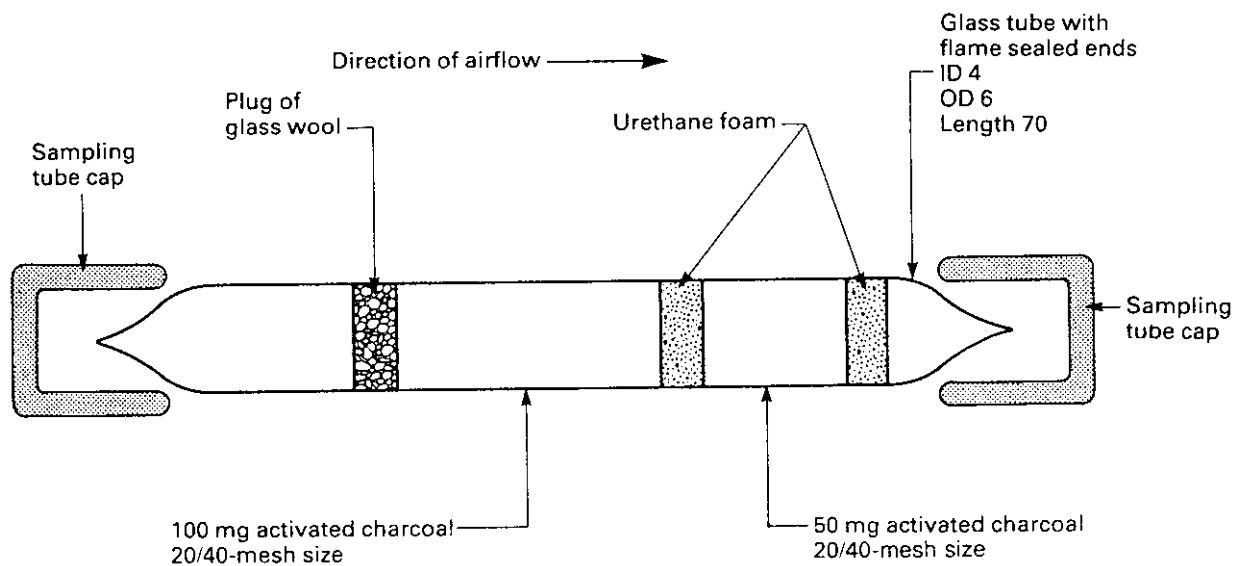
34 Several types of charcoal are commercially available. The products most frequently used for air sampling are derived from coconut shells. The mesh sizes employed vary considerably. NIOSH recommends 20/40 mesh coconut shell charcoal. Severs and Skory<sup>32</sup> found Pittsburgh PCB 12/30 mesh most suitable for

35 Sampling tubes for activated charcoal vary in shape and size. For most applications, HSE and NIOSH recommend tubes measuring 7 cm long with 6 mm o.d. (Figure 3). The tubes contain two sections of 20/40 mesh activated charcoal separated by a 2 mm portion of urethane foam. The front end contains 100 mg of charcoal, the back-up section 50 mg. These tubes are commercially available from many chemical suppliers, and are usually known as 'NIOSH' tubes.

36 Larger tubes are also available that contain 600 mg of charcoal, 400 mg in the front section and 200 mg in the back section; 'jumbo' tubes contain 800 and 200 mg. These tubes are used for the more volatile organic compounds, such as methylene chloride, that have very limited capacity on 100 mg tubes. Other sizes of tube can be ordered or prepared in the laboratory.

37 Sampling tubes need not always be made of glass. Many in use are constructed of stainless steel.

38 The volume of air that can be collected without loss of contaminant depends on the sampling rate, sampling time, volatility of the contaminant, air temperature and humidity, and the concentration of contaminant in the workroom air. For many organic



Dimensions in millimetres

Fig 3

sampling vinyl chloride, vinylidene chloride, and methyl chloride. The final choice for a specific application should be made only after performance and recovery tests have been made.

vapours, a sample volume of 10 litres (1.0 l/min) can be collected without significant loss in 'NIOSH' tubes. A breakthrough of more than 20% into the back-up section indicates some sample loss. Optimum sample volumes

are found in the HSE and NIOSH procedures.

39 The sample volume for gases and highly volatile solvents must necessarily be smaller. A 3% breakthrough was found to occur on 100 mg NIOSH tubes sampling 5 ppm vinyl chloride at 0.2 l/min for 15 minutes. Losses occurred before 5 litres of sample were collected from a 200 ppm vinyl chloride atmosphere at a sampling rate of 50 ml/min.<sup>33</sup>

40 It is always best to refer to an established procedure for proper sampling rates and air sample volumes. In the absence of such information, breakthrough experiments must be performed before field sampling is attempted. Since the sample concentration affects the breakthrough volume, the latter should be determined at the maximum concentration of contaminant expected to be found in the field. (See MDHS 3 and 4<sup>1</sup> for the preparation of known concentrations.) When sampling in the field, the maximum (safe) sampling volume employed should be significantly less than (say half of) the experimental breakthrough volume to allow a safe margin of error.

41 After the procedure has been validated, field sampling may be performed. Immediately before sampling, the ends of the charcoal tube are broken, and the tube placed in a protective holder. Tubing is connected to the back-up end of the charcoal tube (via the holder), and air is drawn through the sampling train with a calibrated suction pump. A personal or area sample may be collected. The duration of the sampling may be several minutes or up to 7-8 hours depending on the tube capacity, the work pattern and the information desired. The air flow should be periodically checked with a flowmeter while the sampling is in progress and at the end of sampling, although this is not essential if a diaphragm pump with stroke counter is used. Afterwards, when sampling is completed, plastic caps or masking tape (but not rubber caps) are placed on the ends of the tube.

42 The first step in the analysis procedure is to remove the contaminant from the charcoal. The most frequently used method of recovery is solvent desorption with carbon disulfide. Unfortunately, carbon disulfide does not completely remove the sorbate from charcoal. Recovery varies for each contaminant and batch of charcoal used. The extent of individual recoveries must be determined experimentally and a correction for desorption efficiency applied to the analytical result.<sup>27</sup> Over a narrow range of analyte concentrations, as used in NIOSH validations,<sup>34</sup> this desorption efficiency is essentially constant, but it may vary widely over larger concentration ranges, particularly for polar compounds.<sup>38</sup> Desorption efficiency can also be affected by the presence of water vapour and of other contaminants.<sup>39</sup> NIOSH<sup>2</sup> recommend that methods should be used only where the desorption efficiency is greater than 75% and ideally should be greater than 90%.

43 The practical desorption step in charcoal analysis is also critical since upon the addition of carbon disulfide to charcoal the initial heat of reaction may drive off the more volatile components of the sample. This can be

minimised by adding charcoal slowly to pre-cooled carbon disulfide. Another technique is to transfer the charcoal sample to vials with Teflon-lined septum caps and to introduce the carbon disulfide with an injection needle. The sealed vial will prevent the loss of any volatilised sample.

44 Several quality assurance schemes have been developed which apply to the charcoal tube method. One of these is the HSE Workplace Analysis Scheme for Proficiency (WASP), details of which may be obtained from the WASP Co-ordinator, HSE, Occupational Medicine and Hygiene Laboratory, Broad Lane, Sheffield S3 7HQ (tel: 0742 892000). NIOSH has a similar scheme<sup>40</sup> linked to accreditation.<sup>41</sup>

### **Silica gel**

45 Silica gel is an amorphous form of silica derived from the interaction of sodium silicate and sulfuric acid. It has several advantages over activated charcoal for sampling gases and vapours: a) polar contaminants are more easily removed from the sorbent by a variety of common solvents; b) amines, nitro-compounds and some inorganic substances for which charcoal is unsuitable can be collected; and c) the use of carbon disulfide is avoided.

46 A disadvantage of silica gel is that it will sorb water. Silica gel is hydrophilic and polar substances are preferentially attracted to active sites on its surface. Water is highly polar and is tenaciously held. If sufficient moisture is present in the air or if sampling is continued long enough, water will displace organic solvents (which are relatively non-polar) from the silica gel surface. With water vapour at the head of the list, compounds in descending order of polarisability are alcohols, aldehydes, ketones, esters, aromatic hydrocarbons, olefins and paraffins. The quantity of humid air that can be effectively passed over silica gel is therefore limited.

47 Nevertheless, silica gel is an effective sorbent for collecting many gases and vapours. Even under conditions of 90% humidity, relatively high concentrations of benzene, toluene and trichloroethylene are quantitatively sorbed on 10 grams of silica gel from air samples collected at the rate of 2.5 litres per minute for periods of at least twenty minutes.<sup>42</sup> Under normal conditions, hydrocarbon mixtures of 2 to 5 carbon paraffins, low molecular weight sulfur compounds (H<sub>2</sub>S, SO<sub>2</sub>, mercaptans), and olefins concentrate on silica gel at dry ice-acetone temperature if the sample volume does not exceed 10 litres. Significant losses of ethylene, methane, ethane and other light hydrocarbons occur if sampling volume is extended to 30 litres.

48 More recent usage, however, has concentrated on smaller sample tubes (in similar sizes to the NIOSH range of charcoal tubes), operated at room temperature.<sup>43,44</sup> NIOSH<sup>2</sup> recommend such tubes for a variety of more polar substances, such as amines, phenols, amides and inorganic acids.

49 Much the same considerations apply to silica gel

tubes as to the charcoal tubes; the sampling capacity and desorption efficiency for the compound of interest should be determined before use, or a reliable officially established method used. A variety of desorption solvents will be needed for desorbing specific compounds with high efficiency; polar desorption solvents, such as water or methanol, are commonly applied.

### Thermal desorption

50 Because of the high toxicity and flammability of carbon disulfide and the labour intensive nature of the solvent desorption procedure, a useful alternative is to desorb the collected analyte thermally.<sup>45-47</sup> Except in a few cases,<sup>32</sup> this is not practical with charcoal as sorbent, as the temperature needed for desorption would result in some decomposition of the analytes. Carbon molecular sieves, or more frequently, porous polymer sorbents, in particular Tenax, Porapak Q and Chromosorb 106, are used instead. Of these, Tenax has the lowest thermal desorption blank (typically less than 0.1 µg per gram of sorbent, when properly conditioned), but only modest sampling capacity compared with carbon.

51 The thermal desorption procedure typically uses larger tubes than the NIOSH method; usually 200-500 mg of sorbent are used, depending on type. Desorption can be made fully automatic and analysis is usually carried out by gas chromatography. Some desorbers also allow automatic selection of sample tubes from a multiple-sample carousel. The whole sample can be transferred to the gas chromatograph, resulting in greatly increased sensitivity compared with the solvent desorption method. Alternatively, some desorbers allow the desorbed sample to be held in a reservoir from which aliquots are withdrawn for analysis, but then the concentrating advantage is reduced.

52 The method has been adopted as a (non-exclusive) recommended method in the UK,<sup>1</sup> Germany,<sup>4</sup> the Netherlands,<sup>48</sup> and Australia<sup>49</sup> but is less widely accepted in the United States.

53 The main disadvantage of thermal desorption directly into an analyser is that it is essentially a 'one-shot' technique; normally the whole sample is analysed. This is why many such methods are linked to mass spectrometry. However, with capillary chromatography it is usually possible to split the desorbed sample before analysis, and if desired the vented split can be collected and re-analysed.<sup>50</sup> Alternatively, the desorbate can be split between two capillary columns of differing polarity.<sup>51</sup>

54 Desorption efficiency is usually 100% for the majority of common solvents and similar compounds in a boiling range of approximately 50-250°C. The analysis of complex mixtures is thus easier than for charcoal or silica gel methods, where a variety of desorption cocktails may be required. On the other hand, if a wide boiling range is to be covered, more than one sorbent may be required. Thus, petroleum may be monitored by a Chromosorb 106 tube and carbon tube in series.<sup>52</sup> An extensive list of recommended sampling volumes and minimum desorption temperatures for Tenax is given in

Brown and Purnell.<sup>47</sup>

### Sampling train

55 Except for grab samplers (paragraphs 10-18) and diffusive samplers (paragraphs 69ff), sampling devices are used in conjunction with a sampling pump and an air metering device or with a diaphragm pump fitted with a stroke counter.

### Pump

56 The pump should have an adjustable flow rate, be capable of being worn by workers while carrying out their normal duties, and be capable of running continuously for 8 hours at the recommended flow rate. The volume of air sampled by the pump over the recommended sampling period should be within 10% ( $\pm 2CV$ ) of the calculated volume. The flow rate should be constant within 5% ( $\pm 2CV$ ) over a period of sampling.

NOTE: The pump should be in accordance with local safety regulations.

### Flow measurement

57 Flowmeters built into pumps are useful guides to constancy of flow and indicators that the pump is working, but they cannot be relied upon for accurate measurement unless suitably calibrated under the conditions of use. The standard for flow measurement should be an external flowmeter whose accuracy is clearly stated by the manufacturer, and preferably traceable to national standards, used with careful attention to the manufacturer's recommendations; or a bubble flowmeter. A bubble flowmeter is an arrangement whereby the pump under test draws a soap film along a calibrated tube. The passage of the film is accurately timed between two marks whose separation defines a known volume. A 1-litre burette can form a suitable tube. The volume between the marks can be checked by filling the burette with distilled water, allowing temperatures to stabilise, drawing off the known volume, and weighing the water, making allowance for the dependence of volume on temperature. A suitable bubble solution can be made by mixing one part of concentrated washing-up liquid, two parts of glycerol, and four parts of water. The burette must be thoroughly wetted with the solution, and several attempts at drawing the film down the tube may be necessary before the tube is wet enough for this to be achieved consistently.

58 The flow standard can be used to calibrate the flowmeter used in the field, which can be the flowmeter incorporated into the pump if this is suitable, or some other portable flowmeter of sufficient precision. NOTE: Inbuilt flowmeters in pumps can overestimate the sample volume if there are leaks in the sampling head or line.

59 For diaphragm pumps, the calibration (ml/stroke)

**Table 4** Some colorimetric procedures for gases and vapours

<i>Gas or vapour</i>	<i>Sampler</i>	<i>Sorbent</i>	<i>Analysis</i>	<i>Reference</i>
Acetaldehyde	Bubbler	Water	Iodoform reaction	53
Acetates	Bubbler	Ethanol	Hydroxamic acid	53
Acetic acid	Wash bottle	Glycerol/water	pH change	53
Acetonitrile	Syringe	Permanganate	Colour change	53
Acrolein	Bubbler	Hexylresorcinol	Spectrophotometry	6
Aldehydes	Bubbler	MBTH	Spectrophotometry	6
Amines	Bubbler	HCl in isopropanol	Ninhydrin/ spectrophotometry	6,53
Ammonia	Bubbler	Dil H <sub>2</sub> SO <sub>4</sub>	Phenol/hypochlorite/ spectrophotometry	6
Aniline	Bubbler	Dil H <sub>2</sub> SO <sub>4</sub>	Spectrophotometry	53
Benzene	U-tube	Silica gel	Spectrophotometry	53
Butanol	Bubbler	Water	Chromate oxidation	53
Carbon disulfide	Glass beads	Copper/ diethylamine	Colour reaction	53
Chlorine	Bubbler	Methyl orange	Spectrophotometry	6
Ethanol	Impinger	Water	Chromate oxidation	53
Formaldehyde	Wash bottle	Water	Chromotropic acid	6
Formaldehyde	Impinger	Bisulfite	Iodine titration	53
Hydrogen sulfide	Bubbler	Iodine soln	Iodine oxidation	53
Mercaptans	Bubbler	Mercuric acetate	Phenylenediamine Spectrophotometry	6
Methanol	Impinger	Water	Fuchsin/ formaldehyde	53
Methyl ethyl ketone	U-tube	Silica gel	Iodoform reaction	53
Methylene bis(phenyl) isocyanate	Impinger	Acid	Diazotization/ coupling/ spectrophotometry	53
Nitrobenzene	Bubbler	Ethanol	Spectrophotometry	53
Nitrogen dioxide	Bubbler	Naphthylethyl-enediamine	Colour reaction	6,53
Nitromethane	Bubbler	Phosphate	Diazotization coupling/ spectrophotometry	53
Ozone	Impinger	KI	Titration	53
Phenol	Impinger	Ethanol	Spectrophotometry	53
Phenol	Impinger	NaOH soln	Aminoantipyrene/ spectrophotometry	6
Pyridine	Bubbler	Ethanol	Spectrophotometry	53
Sulfur dioxide	Impinger	Tetrachloro-mercurate	Spectrophotometry	6,53
Toluene	U-tube	Silica gel	Spectrophotometry	53
Toluene diisocyanate	Impinger	Acid	Diazotization/ coupling/ spectrophotometry	53

should be checked regularly at a selection of flow rates against a wet gas meter.

#### Analysis of gases and vapours

60 No attempt is made to provide a complete list of analytical procedures. Table 3 provides pertinent analytical information for the collection of a number of organic vapours on charcoal tubes, as found in the HSE MDHS methods.<sup>1</sup> Table 4 lists some gases and vapours that may be analysed by wet chemical methods or by ultraviolet spectrophotometry, and is a selection from two primary compendia of methods, from the AIHA Analytical Chemistry Committee<sup>53</sup> and the Intersociety Committee.<sup>6</sup> Source references are given in these compendia. Other useful sources are Hanson,<sup>54</sup>

Jacobs,<sup>55-56</sup> the MDTSA series,<sup>57</sup> Ruch<sup>58-59</sup> and Thomas.<sup>60</sup> Spectrophotometric methods have now largely been replaced by direct-reading instruments or detector tubes or by high-performance liquid chromatography (HPLC) or other instrumental techniques.<sup>1-2</sup> However, they still have their place, particularly for highly reactive species such as isocyanates,<sup>24</sup> chlorine, and formaldehyde.<sup>61</sup>

#### Calculations

61 The collected sample is analysed, either directly if a gas phase or impinger sample, or after desorption if

collected on a solid sorbent, using appropriate gas or liquid standard solutions to calibrate the analytical instrument. Gas phase samples give a result directly in ppm (v/v), but other types of sample will give a mass of analyte per collected sample, or a concentration, which can be converted to a mass by multiplying by the sample volume.

62 The mass concentration of the analyte in the air sample is then calculated as follows:

**Impinger**

$$C = \frac{(m - m_{\text{blank}})}{SE \times V} \quad (2)$$

- where:
- C = mass concentration of analyte in air (mg/m<sup>3</sup>)
  - m = mass of analyte in sample (µg)
  - m<sub>blank</sub> = mass of analyte in blank (µg)
  - SE = sampling efficiency
  - V = volume of air sampled (litres)

**Sorbent tube**

$$C = \frac{(m_1 + m_2 - m_{\text{blank}})}{DE \times V} \quad (3)$$

- where:
- m<sub>1</sub> = mass of analyte on first tube section (µg)
  - m<sub>2</sub> = mass of analyte on back-up tube section (if used) (µg)
  - DE = desorption efficiency corresponding to m<sub>1</sub>

NOTE: If it is desired to express concentrations reduced to specified conditions, eg 20°C and 101 kPa, then

$$C_{\text{corr}} = C \times \frac{101}{P} \times \frac{T + 273}{293} \quad (4)$$

- where:
- P = actual pressure of air sampled (kPa)
  - T = actual temperature of air sampled (°C)

**Volume fraction**

The volume fraction of the analyte in air, in ppm (v/v), is

$$C' = C_{\text{corr}} \times \frac{24.05}{MW} \quad (5)$$

where: MW = molecular mass of the analyte of interest (g/mol)

**DIFFUSIVE SAMPLERS**

**Introduction**

63 A diffusive (or 'passive') sampler is a device which is capable of taking samples of gas or vapour pollutants from the atmosphere at a rate controlled by a physical process such as diffusion through a static air layer or permeation through a membrane, but which does not involve the active movement of the air through the sampler.<sup>62</sup>

64 The theoretical basis for diffusive sampling is now well established.<sup>62</sup> Diffusion and permeation processes can both be described in derivations of Fick's first law of diffusion (equation 6), which result in expressions relating the mass uptake by the sampler to the concentration gradient, the time of exposure, and the sampler area exposed to the pollutant atmosphere.<sup>63</sup> Expressions have also been derived for the application of Fick's law to diffusive sampling in the 'real' world, ie taking into account non-steady state sampling, the effects of fluctuating concentrations, sorbent saturation, wind velocity and turbulence at the sampler surface, temperature, pressure and so on.<sup>64-65</sup> Except for sorbent saturation, which may lead to reduced (although sometimes predictable) uptake rates, these modifications to the basic Fick's law expression do not lead to significant errors for well-designed samplers, and such samplers may be regarded as truly integrating devices with accuracies similar to those of active samplers.

65 A variety of diffusive samplers have been described.<sup>66-70</sup> Typical designs are shown schematically in Figure 4. Diffusive equivalents to the more familiar pumped methods exist for nearly all types; the main exception being the direct collection of gas samples, where the nearest equivalent is an evacuated canister. Thus the diffusive equivalent of an impinger is a liquid-filled badge such as the Pro-Tek (TM) inorganic monitor or the SKC badge; the diffusive equivalent of the charcoal tube is the charcoal badge such as the 3M OVM or the MSA VaporGard organic; and the diffusive equivalent of the thermal desorption method is the Perkin-Elmer tube or the SKC thermal desorption badge. There are also diffusive devices based on reagent-impregnated solid supports, but these are mostly direct-reading and are not covered in this document.

66 In general, the Regulatory Authorities have been reluctant to accept diffusive monitoring methods, except in the UK and the Netherlands, where several such methods have been adopted as non-exclusive recommended methods.<sup>1,48</sup> However, the Luxembourg Symposium<sup>62</sup> concluded that:

The theoretical basis for diffusive sampling has been confirmed by laboratory and field trials.

Active and diffusive sampling are complementary approaches each one having areas of applicability

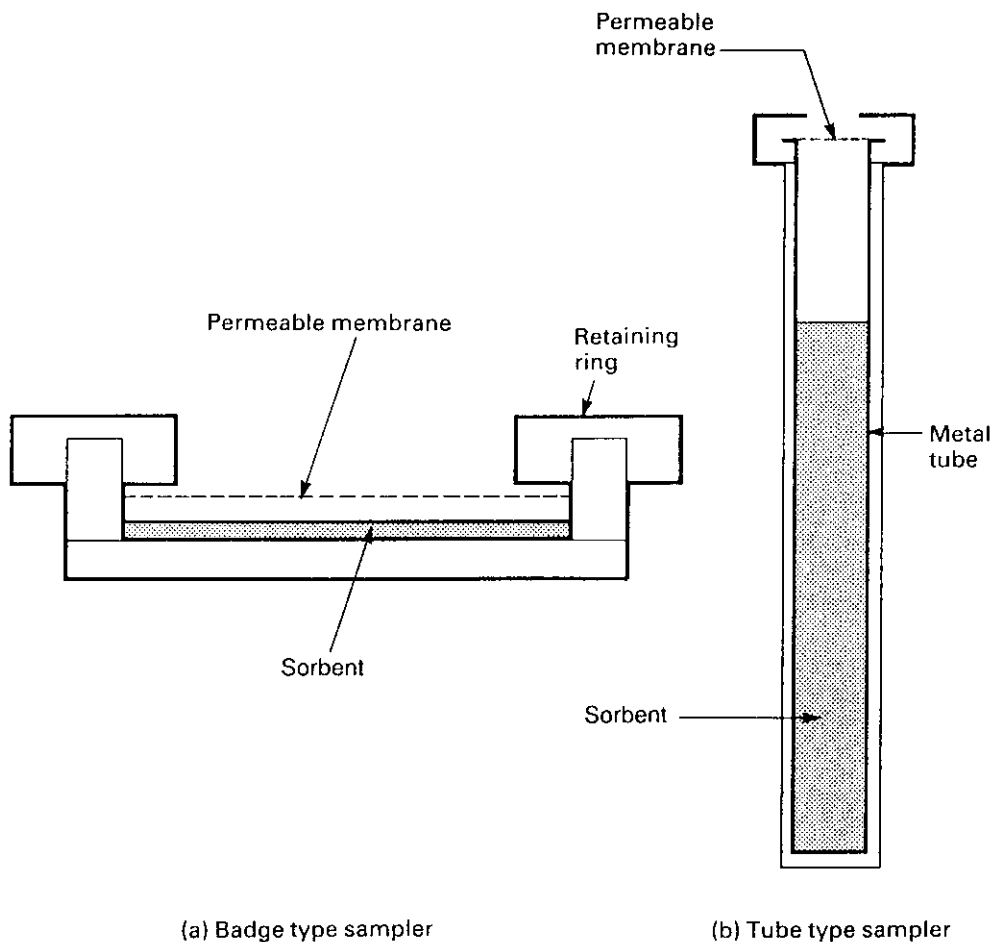


Fig 4

which may overlap. Each has its role in a strategy for monitoring workers' exposure. In general there seems to be no significant difference between the accuracy and precision of diffusive sampling and those of other monitoring systems such as active pumped sampling.

It was agreed that as a general principle, any method is acceptable by regulatory authorities and hygienists if used by experts within its defined limitations. This applies equally to diffusive samplers.

67 The Symposium also concluded:

Validation of all sampling systems is essential both in the laboratory and in the field

and it is recommended that an established evaluation protocol be followed, such as NIOSH<sup>71</sup> or HSE.<sup>72</sup>

**Calibration**

68 The basic expression of Fick's law is:

$$J = D(C_o - C_e) / L \quad (6)$$

and

$$Q = DA t (C_o - C_e) / L \quad (7)$$

- where:
- J = diffusive flux (g/cm<sup>2</sup>.sec)
  - D = coefficient of diffusion (cm<sup>2</sup>/sec)
  - A = cross sectional area of diffusion path (cm<sup>2</sup>)
  - L = length of diffusion path (cm)
  - C<sub>o</sub> = external concentration being sampled (g/cm<sup>3</sup>)
  - C<sub>e</sub> = concentration at the interface of the sorbent (g/cm<sup>3</sup>)

$$\begin{aligned} Q &= \text{mass uptake (g)} \\ t &= \text{sampling time (sec)} \end{aligned}$$

69 It is apparent from an inspection of these equations that the expression  $DA/L$  has units of  $\text{cm}^3/\text{sec}$  and therefore represents what can be considered as a 'sampling rate' of the diffusive sampler when comparing to a pumped sampling system. This simple use of the sampling rate concept has proven of considerable value to users of the devices and is often expressed in the dimensionally equivalent units of  $\text{ml}/\text{min}$ . Knowledge of the geometry of the sampler (which will be fixed for any given sampler type) permits the calculation of the sampling rate provided the diffusion coefficient is known. A number of manufacturers have published tables of sampling rates calculated in this way, most of whom have used the same source of published diffusion coefficients.<sup>73</sup> Diffusion coefficients that are not in this list can be calculated theoretically.<sup>74</sup>

### Environmental factors affecting monitor performance<sup>62,69-72</sup>

#### Temperature and pressure

70 From Maxwell's equation, the diffusion coefficient,  $D$ , is a function,  $f$ , of absolute temperature and pressure:

$$D = f(T^{1.5}, P^{-1}) \quad (8)$$

But from the general gas law:

$$\begin{aligned} PV &= nRT \\ C &= n/V = P/RT \quad (9) \end{aligned}$$

Substituting (8) and (9) in (7), we get:

$$\begin{aligned} Q &= f(P/T, T^{1.5}/P) \\ &= f(T^{0.5}) \quad (10) \end{aligned}$$

Thus  $Q$  is independent of pressure,  $P$ , but dependent on the square root of absolute temperature,  $T$ . In practice, the temperature dependence of the sampling rate at ambient temperature levels (about 0.2% per °C) may be ignored. However, temperature may affect the capacity of a sorbent adversely.

#### Humidity

71 High humidity can affect charcoal adsorption adversely, resulting in a reduction in saturation capacity for charcoal badges. If the sampler becomes saturated,  $C_e$  in equation 6 is no longer zero, and the sampling rate becomes non-linear. Porous polymers used for thermal desorption are relatively unaffected by humidity.

#### Transients

72 Simple derivations of Fick's law assume steady-state conditions, but in the practical use of such samplers, of course, the ambient concentrations of pollutants are likely to vary widely. The question then arises whether a diffusive sampler will give a truly

integrated response, or will 'miss' short-lived transients before they have had a chance to diffuse into the sampler. The problem has been discussed theoretically<sup>68,75-76</sup> and practically.<sup>77-78</sup> Generally, transients do not present a significant problem provided the total sampling time is well in excess of the time constant of the sampler, ie the time a molecule takes to diffuse into the sampler under steady-state conditions. The time constant of most commercial samplers is between 1 and 10 secs.

#### Sorbent factors

73 All diffusive samplers rely on sorbents having a high affinity for the contaminant being sampled, ie  $C_e = \text{zero}$  in equation 6 and uptake is linearly proportional to concentration and time of exposure. Useful checks on sorbent suitability are a back-diffusion test given in Bartley<sup>79</sup> and the measurement of adsorption isotherms.<sup>80</sup>

#### Face velocity

74 Diffusive samplers also rely on the external concentration, ie  $C_o$  in equation 6, being maintained at the sampler surface. In the absence of sufficient air movement across the face of the sampler, transport of pollutant to the surface may itself be limited by diffusion and the effective sampling rate will be reduced. At the other extreme, very high air velocities may induce turbulence within the sampler body if the draught shield is inadequate; the effective diffusion path length will be reduced and the sampling rate increased. The magnitude of these effects will vary with the geometry and design of particular samplers, although for the majority of modern samplers, sampling rates are reasonably constant within the range of air velocities likely to be encountered in workplace personal monitoring. Samplers with a large surface area ('badge' types) should not be used in 'static' positions, where air velocities may be below their critical values for this type of sampler (about 0.2 m/s).

#### Calculations

75 The method of calculation of atmospheric concentrations is essentially the same as for pumped samplers, ie the collected sample is analysed and the total mass of analyte on the sampler determined.

Then, as before:

$$C = \frac{(m_1 + m_2 - m_{\text{blank}})}{DE \times V} \quad (3)$$

( $m_2$  and  $DE$  are ignored for liquid sorbent badges).

$V$ , the total sample volume, is calculated from the effective sampling rate (litres/min) and the time of exposure (min).

76 This calculation gives  $C$  in  $\text{mg}/\text{m}^3$ , and strictly speaking, an appropriate sampling rate for the ambient

temperature and pressure should be made, as equation 9 assumes C is in ppm.

77 Alternatively, sampling rates can be expressed in units such as ng/ppm/min (dimensionally equivalent to cm<sup>3</sup>/min), when C' is calculated directly in ppm:

$$C' = \frac{(m_1 + m_2 - m_{\text{blank}})}{DE \times U \times t'} \times 1000 \quad (11)$$

where: U = sampling rate (ng/ppm.min)  
t' = sampling time (min)

NOTE: m<sub>2</sub> is relevant only to samplers with a back-up section, and an additional multiplication factor may be needed to account for differing diffusion path lengths to primary and back-up sections.

### Accuracy of diffusive monitoring

78 The overall accuracy of diffusive monitors has been studied extensively.<sup>62</sup> Brown,<sup>81</sup> for example, examined the Perkin-Elmer tube for acrylonitrile, benzene, butadiene, carbon disulfide and styrene and found the sampler to be at least as accurate as the equivalent pumped method. Laboratory precision was, on average, 10% for the diffusive sampler. Field precision was 12% for the diffusive sampler and 13% for the pumped sampler. Kennedy<sup>82</sup> evaluated a range of inorganic samplers, including 3M, Dupont, MSA, REAL and SKC samplers, and found they generally met NIOSH criteria.

79 A European interlaboratory comparison<sup>83</sup> of the 3M badge exposed to butanol, pentanal, trichloroethane, octane, butyl acetate, 3-heptanone, xylene, α-pinene and decane showed generally good agreement with the charcoal tube. Exceptions were butanol and pentanal, where the diffusive samplers read low. Overall laboratory precision, again excluding butanol and pentanal, varied between 9% (xylene) and 13% (heptanone). The contribution of interlaboratory error was less than half of these values.

80 Field and laboratory test results on the Pro-Tek organic monitor have been published by Lautenberger et al,<sup>84</sup> including data on acrylonitrile, benzene, carbon tetrachloride, acetone and toluene. In comparative testing, the badge demonstrated an overall accuracy at least as good as the charcoal tube method.

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