MDHS

Methods for the Determination of Hazardous Substances

Health and Safety Laboratory

HSE
Health & Safety Executive

88

Volatile organic compounds in air

Laboratory method using diffusive samplers, solvent desorption and gas chromatography

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INTRODUCTION

Requirements of the COSHH Regulations

1 The Control of Substances Hazardous to Health (COSHH) Regulations[1] are designed to ensure that the exposure of people at work to substances which could cause health damage is either prevented, or where that is not reasonably practicable, adequately controlled. Employers are required to make an assessment of the health risk created by such work, and to prevent or control exposure to the substances involved. The COSHH regulations also require that persons who may be exposed to substances hazardous to health receive suitable and sufficient information, instruction and training. Employers must ensure that their responsibilities under the COSHH Regulations are fulfilled before allowing employees to undertake any procedure described in this MDHS.

Analytical methods

2 This is not a 'reference' method in the strict analytical sense of the word. It is a method compendium applicable to a number of volatile organic compounds. There may be alternative methods available for the determination of a particular analyte. With the exception of a few cases, where an exposure is linked to a specific method (eg rubber fume or asbestos), the use of methods not included in the MDHS series is acceptable provided they have been shown to have the accuracy and reliability appropriate to the application.

3 Procedures described in this method compendium have been validated for some designated compounds to demonstrate that they comply with *Workplace atmospheres - requirements and test methods for diffusive samplers for the determination of gases and vapours*[4] described by the Comité Européen de Normalization (CEN) in European Standard BS EN 482. If an alternative method is used it is necessary to determine and state performance parameters for that method.

Quality control

4 An appropriate level of quality control should be employed when using this method compendium. Guidance is given in MDHS 71.[3] The long-term stability of hydrocarbons and some chloroalkanes on charcoal is good. The long-term stability of many polar compounds on charcoal is unknown. It is strongly advised that analysts participate in an external quality assurance scheme. Satisfactory performance in WASP or the NIOSH PAT schemes would give added confidence in performing methods based on this method compendium.

PRINCIPLE

5 Diffusive samplers consist of a sorbent separated from ambient air by some form of diffusion resistance, commonly a controlled air gap and draught shield. The diffusive sampler is exposed to air for a measured time period. The rate of sampling for a specific compound is determined by prior exposure in a standard atmosphere. Volatile organic compounds migrate into the sampler by diffusion and are collected on the sorbent (normally activated carbon). The collected vapour is desorbed by a solvent (typically carbon disulphide), and the solution is analysed with a gas chromatograph equipped with a flame ionisation detector, mass spectrometer or other selective detector.

SCOPE AND FIELD OF APPLICATION

6 This compendium applies to diffusive samplers containing a sorbent (normally activated carbon) used for the determination of the time-weighted average concentrations of volatile organic compounds (VOCs) in workplace atmospheres. Of samplers that are known to be commercially available, those manufactured by Dräger, 3M and SKC are qualitatively similar. The geometry is that of a tube (Dräger ORSA-5) or badge

(3M 3500, SKC-575) and the diffusion path is axial to the packed bed or disc of sorbent. In the Radiello device, diffusion is radial to the surface of a coaxial sorbent cartridge. Uptake rates depend on the ratio of the effective exposed area to the linear dimension of the air gap (A/L). Uptake rates are in the range of: Dräger ORSA-5, 4-8 $cm^3\ min^{-1}$; SKC-575, 9-18 $cm^3\ min^{-1}$; 3M-3500, 20-40 $cm^3\ min^{-1}$; Radiello, 40-90 $cm^3\ min^{-1}$.

7 The diffusive samplers described here are supplied pre-packed and ready to use. A pre-paid analysis service is sometimes provided, subject to certain limitations and depending on country of purchase. Manufacturers' validation data are available for a range of compounds. Data for other samplers may be included in future revisions of this compendium.

8 Procedures described in this compendium are generally valid for the measurement of airborne VOC vapour in the concentration range of approximately 1-1000 mg m^{-3} of VOCs for exposure times between 30 min and 8 hr. The upper limit of the exposure dose (mg m^{-3} x hr) depends on the sorptive capacity of the carbon or other sorbent for specific VOCs and on the linear dynamic range of the gas chromatographic column and detector. The lower limit of the exposure dose depends on the noise level of the detector and on blank levels of analyte on the sorbent.

9 HSE Guidance Note EH42[37] advises employers about how they should conduct investigations into the nature, extent and control of substances hazardous to health which are present in workplace air. The objective of air monitoring is usually to determine worker exposure and therefore the procedures described in this method compendium are for personal sampling in the breathing zone. They may also be used for background or fixed location monitoring if sufficient air movement can be assured. Sampling times shorter than 30 min might be feasible, depending on design. Where the instantaneous concentration value is fluctuating, measurement of mean concentration is valid, provided the total sampling time exceeds the time constant of the device by an adequate margin. For samplers described in this method compendium, the lower limit may be in the range 5-10 min, although 30 min is usually the shortest time used in validation studies. Alternative on-site procedures, such as portable gas chromatography, infra-red spectrophotometry or a total organic analyser, may be used to monitor rapidly changing concentrations of single substances or mixtures.

Interferences

10 Organic components that have the same or nearly the same retention time as the analyte of interest during the gas chromatographic analysis will interfere where a non-selective detector is used. Interferences can be minimised by proper selection of gas chromatograph columns and conditions.

11 High humidity may affect the recovery of some compounds from samplers, particularly for those using activated charcoal. Manufacturers' data sheets should be consulted for specific advice.

Overall uncertainty

12 The overall uncertainty for a measuring procedure is defined in BS EN 482[38] as 'the quantity used to characterise as a whole the uncertainty of the result given by a measuring procedure', and is quoted as a percentage combining bias and precision using the following equation where:

$$\text{Overall uncertainty} = \frac{\left|\overline{x} - x_{ref}\right| + 2s}{x_{ref}} \times 100$$

$\overline{x}$ is the mean value of results of a number n of repeated measurements;

x_{ref} is the true or accepted reference value of concentration;

s is the standard deviation of measurements.

The performance requirements quoted in BS EN 482 for overall uncertainty, where the task is 'measurement for comparison with limit values', are ≤50% for samples in the range 0.1 to 0.5 LV and ≤30% for samples in the range 0.5 to 2.0 LV (LV = Limit Value).

13 Procedures included in this compendium have been examined in accordance with the diffusive sampler evaluation protocol EN 838:1995[4] or close equivalent,[5] using several test compounds. For the purposes of this method, the NIOSH protocol[6,7] is equivalent to EN 838. EN 838 assigns levels of evaluation defined as:

> 1A: Full evaluation of uptake rate, including effects of time, concentration, humidity, back-diffusion, storage, desorption efficiency and air velocity; overall uncertainty combining bias and precision errors ≤30% for samples in the range 0.5 to 2.0 LV.
>
> 1B: Partial evaluation of an analogue within a homologous series in which upper and lower members have been shown to comply with level 1A.

Evaluations to EN 838 level 1A or 1B are time consuming. This method compendium acknowledges that in the absence of experimental data, empirical data based on the ideal uptake rate could be used, subject to certain limitations. Tables 1 and 2 summarise the levels of evaluation as follows:

> A: Full (EN 838 level 1A or NIOSH protocol or close equivalent).
>
> B: Partial (EN 838 level 1B, or other tests in which experimental uptake rates were measured over a more limited range than that specified by level 1A or 1B, as described in EN 482:1994[8]).
>
> C: Theoretical or ideal uptake rates calculated from known or estimated diffusion coefficients and a geometric constant characteristic of the

sampling device (the ratio of the effective area to the diffusion path length, A/L cm). The geometric constant may itself be estimated from selected experimental diffusion coefficients and uptake rates if the device moderates diffusion through a porous barrier or operates by radial diffusion.

14 There is no general consensus on the tests to be included in a partial type B evaluation. The significance of certain tests, such as back-diffusion or desorption efficiency, depends on the type of sampler and the application. One manufacturer (SKC Inc) distinguishes between its evaluation of an analogue within a homologous series, designated 'bi-level', in which the lower member complies fully with EN 838 level 1A, and more limited tests designated 'partial'.[7] For the purposes of this method, field evaluations can also comply with type B, subject to comparison of the sampler with an independent method which has also been validated according to an established protocol, eg a pumped sorbent tube or a different diffusive sampler method.

Note: Precision and related terms are as defined in ISO 5725[9] or by IUPAC.[10]

Uptake rates

15 Diffusive uptake rates for samplers supplied by Dräger, 3M and SKC samplers are given in Table 1. Uptake rates for the Radiello tube are listed in Table 2. Data on approximately 200 compounds have been compiled from the manufacturers' latest sources available.[11-16] Uptake rates listed as type C evaluation were calculated by the manufacturers using geometric constants and diffusion coefficients either known experimentally[17] or estimated from empirical equations.[18-21] Additional data may be included in later revisions of this method.

Note: The Dräger ORSA-5 effective A/L ratio has been revised from 1.41 cm to 1.25 cm (0.80 cm^{-1}). Manufacturer data in Table 1 are the latest available and have been adjusted relative to published data in references 11-13.

16 The uptake rate of samplers is not significantly affected by air movement, provided the air velocity exceeds a threshold value which depends on design. Generally, air velocities greater than 0.1 m s^{-1} are sufficient for the samplers cited in paragraph 15. Controlled chamber studies up to 2.5 m s^{-1} have found no significant effect on uptake, but characteristics of other samplers may vary.[22] Very high air velocities may have an effect with some designs.[39] Manufacturer documentation should be consulted for any specific recommendations.

17 The temperature-dependence of mass uptake is expected to be small (+0.2% per $^{\circ}C$ increase in ambient temperature), if non-ideal sorption effects are ignored.

REAGENTS

18 During the analysis, use only reagents of recognised analytical grade if possible.

Calibrants

19 Most analytes listed in Tables 1-2 are commercially available in at least 98% purity. Where only technical grades of 90-95% can be obtained for calibration standard preparation, consider either correction from a purity measurement before use or purification by, eg, fractional distillation.

Note: Water as an impurity is not measured by the flame ionisation detector. If significant water content is suspected, it is recommended that gas chromatography-mass spectrometry (GC-MS) is used for purity measurements, or if an MS detection is not feasible, a thermal conductivity detector could be substituted.

Desorption solvents

20 The desorption or elution solvent, commonly carbon disulphide, should be of chromatographic quality. It must be free from compounds co-eluting with the substances of interest. Suitable high-purity carbon disulphide (benzene <1 µg mL^{-1}) is commercially available from Aldrich Chemical Co, J T Baker, Fluka Chemie and other sources. Carbon disulphide is normally recommended for the desorption of non-polar compounds from activated carbon.

21 For polar compounds and mixtures of polar and non-polar compounds there is no ideal universal desorption solvent. Dichloromethane, methanol, higher alcohols, dimethyl formamide, dimethyl sulphoxide and acetonitrile have been used as eluants, either singly or mixed with each other or carbon disulphide. OSHA method 07 (organic vapours)[23] and the NIOSH methods 1301, 1400, 1401, 1402, 1403 for ketones and alcohols[24] give examples of suitable desorption solvents other than pure carbon disulphide. A recent study of mixed solvents adsorbed on charcoal[36] concluded that 4% dimethyl sulphoxide in carbon disulphide gave adequate recovery for most glycol ethers (>75%) and good recovery of most hydrocarbons, ketones and esters (>90%).

APPARATUS

Ordinary laboratory apparatus and:

Diffusive samplers

22 A number of solvent-desorption diffusive samplers are available commercially. Samplers used in evaluating this method are listed in paragraph 15. The list is not complete. It should not be taken as indicating a preference for these particular devices. Other types of diffusive sampler based on the solvent desorption principle are commercially available. They may be more or less suitable, depending on the application, but are likely to have slightly different performance characteristics. Details of all those known to be commercially available in Europe are given in the Appendix.

Gas chromatograph

23 A gas chromatograph fitted with a flame ionisation detector is suitable. In some applications, involving the analysis of complex mixtures, a high-resolution capillary column and a selective detector or mass spectrometer may be required. Alternatively, if these detectors are not available, two columns with phases of different polarity may be connected in parallel to one injector. A wide range of gas chromatographic columns are capable of separating the analytes of interest from other components. Suitable choices might be a 50 m x 0.22 mm fused silica capillary coated with dimethylsiloxane (eg BP-1) or 7% cyanopropyl, 86% methyl siloxane (eg BP-10) at 0.5-1.0 µm film thickness.

Note: BP-1 and BP-10 are proprietary phases of SGE Ltd. Some examples of equivalent phases are SPB-1 and SPB-1701 (Supelco), HP-1 and HP-1701 (Hewlett-Packard), CP-Sil 5CB and CP-Sil 19CB (Chrompack).

Autosampler

24 These are commercially available with liquid-chilled sample trays, suitable for the analysis of volatile solvents.

Integrator

25 The sensitivity and dynamic range of the integrator should correspond to that of the detector output and its sampling frequency must be sufficient to measure peak areas with appropriate precision.

PROCEDURE

Note: The following summaries are sufficient for an experienced analyst to perform the method in most cases. Manufacturers may supply more detailed guidance with their samplers.

Collection of samples and desorption (for 3M 3500)

26 Immediately before sampling, remove the diffusive sampler from its protective metal can. When used for personal sampling, the sampler should be mounted in the worker's breathing zone, for example on the lapel. Ensure that when mounted, the sampler is freely open to the atmosphere, ie it is not obscured by clothing or other objects. At the end of a measured time period of exposure, the sampler is removed, and the white membrane and retaining ring removed and replaced by the closure cap with the ports firmly closed. The sampler is then replaced in its protective metal can for transport.

27 Desorption should be carried out in a clean atmosphere in a fume hood. The centre port on the closure cap is opened and 1.5 mL of elution solvent is pipetted into the sampler. The port is closed and the sampler is agitated occasionally over a period of 30 min to ensure maximal desorption. Desorb the sample blank in the same way.

Collection of samples and desorption (for Dräger ORSA-5)

28 Immediately before sampling, remove the diffusive sampler from its transportation jar and place in the holder. When used for personal sampling, the sampler should be mounted in the worker's breathing zone, for example on the lapel. Ensure that when mounted, the sampler is freely open to the atmosphere, ie it is not obscured by clothing or other objects. At the end of a measured time period of exposure, remove the sampling tube from its holder and return it to the transportation jar. Seal the jar carefully with the screw cap.

29 Desorption should be carried out in a clean atmosphere in a fume hood. The sampling tube is removed from the transportation jar. One of the exposed porous plugs is also removed and the charcoal sorbent tipped carefully into a septum vial (5-15 mL). The vial is closed and elution solvent (2-10 mL, depending on application) added through the septum. The vial is agitated occasionally over a period of 30 min to ensure maximal desorption. Desorb the sample blank in the same way.

Collection of samples and desorption (for SKC-575)

30 Immediately before sampling, remove the diffusive sampler from its protective bag. When used for personal sampling, the sampler should be mounted in the worker's breathing zone, for example on the lapel. Ensure that when mounted, the perforated face of the sampler is freely open to the atmosphere, ie it is not obscured by clothing or other objects. At the end of a measured time period of exposure, the sampler is removed and sealed as follows: place the o-ring provided on the sampler face and press on the cover, ensuring the o-ring is sealed all round. Send the sampler together with the remaining accessories (including the operating instructions) to the analysing laboratory.

31 Desorption should be carried out in a clean atmosphere in a fume hood. Do not remove the cap from the face of the sampler. Open the two ports at the rear using a sharp knife or other means. Slowly pipette 2.0 mL of elution solvent into the sampler. Press the plugs into place to close the ports and desorb for one hour using shaker model 226D-03-1 (SKC Inc) or equivalent. Open the ports and either remove aliquots for direct syringe injection or transfer the elution solvent to an autosampler vial through the length of PTFE tube provided (see operating instructions). Approximately 1.5 mL can be transferred by the latter method.

Collection of samples and desorption (for Radiello)

32 Immediately before sampling, remove the sorbent cartridge from its glass storage tube and insert in the diffusive body, taking care not to touch the cartridge with the fingers. A practical way of doing this is to hold the body and storage tube with their open faces together and turn upside down, while keeping them close to each other. Check that the cartridge is correctly seated in the body. The top edge of the cartridge must be flush with the

top of the screw-thread in the body. Gently tap the body if it is not. Screw the body onto the support plate while holding it upwards, so as to maintain the cartridge in the correct position. When used for personal sampling, the sampler should be mounted in the worker's breathing zone, for example on the lapel. Ensure that when mounted, the sampler is freely open to the atmosphere, ie it is not obscured by clothing or other objects. At the end of a measured time period of exposure, unscrew the diffusive body from the support plate. Remove the sorbent cartridge and replace in the storage tube by turning the diffusive body upside down.

33 Desorption should be carried out in a clean atmosphere in a fume hood. Remove the cap from the storage tube and pipette in 2.0 mL elution solvent. Leave for at least 30 min, occasionally agitating to ensure maximal desorption. Remove the cartridge from the solvent after 2 hr if the analysis is delayed.

Blanks

34 All sample blanks should be prepared subjecting samplers to the same handling procedure as the exposed samplers, except for the actual period of exposure. It is recommended that blank and exposed cartridges be taken from the same package. Two extra cartridges are supplied for this purpose with each complete sampler set.

Preparation of standard solutions

35 A standard solution of the compounds of interest in the elution solvent may be prepared gravimetrically, using either a microsyringe or pipette, by adding pure compounds or pre-weighed blends to flasks partially filled with the elution solvent. Where small quantities of a few microlitres are added to partially-filled flasks, it is recommended that the pure compounds or blends are injected through a silicone septum, such as a Suba-Seal®. Further standard solutions to cover the range of interest can be prepared by serial dilution of the first solution. The concentration range of the standard solutions should exceed the concentration range of the desorbed samples. Prepare fresh standard solutions with each batch of samples.

36 The purpose of gravimetry is to avoid the need for calibration of volumetric apparatus and to reduce errors caused by evaporation of very volatile compounds; however, it is common practice to use some combination of gravimetry and volumetry, or pure volumetry, in the preparation of standard solutions. It is acceptable to use volumetry, provided that the apparatus is calibrated appropriately with the liquids actually used in the analysis. The use of some volumetric apparatus certified with mercury or water, particularly microsyringes and pipettes, can give errors of up to ±3%.

37 An internal standard is optional. In the context of this method, the purpose of the internal standard is to correct for small variations in the injection volume. Autosamplers normally reduce the need for an internal standard. It must not interfere with the compounds of interest and it must not be removed from the elution solvent by the sorbent. The use of an internal standard as a surrogate to correct for desorption efficiency (eg n-propyl acetate in the analysis of n-butyl acetate) is not normally recommended. Desorption efficiency should be determined directly with the compounds of interest (paragraphs 45-51).

38 In the analysis of complex mixtures, calibration blends of the pure compounds may be prepared before dilution with the elution solvent. Examples of three calibration blends are listed here. These have been used in the analysis of mixed solvents in paints, thinners, adhesives, cleaning fluids and miscellaneous commercial products. The components are arranged to give resolved peaks on both BP-1 and BP-10 phases. Other blends may be more appropriate on different columns or in other applications.

Blend 1 consists of: n-hexane, n-heptane, n-octane, n-decane, n-undecane, n-dodecane, benzene, toluene, o-xylene, p-xylene, n-propylbenzene, iso-propylbenzene, o-ethyltoluene, m-ethyltoluene, p-ethyltoluene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, n-propyl acetate, n-butyl acetate, iso-butyl acetate, butoxyethyl acetate.

Blend 2 consists of: iso-propanol, iso-butanol, n-butanol, 1-methoxy-2-propanol, butoxyethanol, toluene, ethylbenzene, 1,2,3-trimethylbenzene, ethyl acetate, ethoxyethyl acetate.

Blend 3 consists of: acetone, 2-butanone, 4-methylpentan-2-one, cyclohexanone, 2-methylcyclohexanone, 3-methylcyclohexanone, 4-methylcyclohexanone, iso-propyl acetate, n-nonane, toluene.

Stability of calibration blends

39 In the above examples, calibration blends 1-3 are stable for at least one year when stored in dark glass bottles with PTFE-lined screw-caps at less than 4°C. Storage times for calibration solutions vary according to application. Typically, carbon disulphide dilutions should be prepared fresh weekly, or more frequently if evidence is noted of decomposition or evaporation.

Analysis

40 Inject into the gas chromatograph a known fixed volume of each standard solution in the range 1-5 µL. A standardised injection technique should be used so that repeatable peak heights or areas are obtained. Typically, for a series of replicate injections, the relative standard deviation should be better than ±2%. Autosamplers normally achieve better than ±1%.

41 Prepare a log-transformed calibration graph by plotting the $_{10}$logarithm of the areas of the analyte peaks corrected for blank levels on the vertical scale against the $_{10}$logarithm of the concentration of the analyte, in µg mL^{-1}, in the injected aliquot of the calibration blend solutions. Other methods of weighting calibration points, such as linear, exponential or polynomial plots, may be more or

less suitable, depending on the linearity of the detector response and the software available.

42 Inject into the gas chromatograph the same fixed volume of solution from the desorbed sample. Read from the calibration graph the concentration of the analyte in the desorbed sample. Analyse the sample blank and the samples used to determine desorption efficiency in the same way.

43 Set up the gas chromatograph for the analysis of volatile organic compounds. A variety of chromatographic columns may be used for the analysis of these compounds. The choice will depend largely on which compounds, if any, are present that might interfere in the chromatographic analysis. Examples of suitable choices are 50 m x 0.22 mm fused silica columns with thick-film BP-1 or BP-10 stationary phases. Typical operating conditions for these columns might be temperature programming from 50-200°C at 5°C min^{-1} with a carrier gas flow of 0.7-0.8 mL min^{-1} helium.

44 Correspondence of retention time on a single column should not be regarded as proof of identity. The retention indices of about 160 VOCs on BP-1 and BP-10 phases are given in Table 3. They are a useful guide to elution order on these phases or their near equivalent, but are not definitive, since exact values depend on temperature programme, carrier flow-rate and other factors.

Determination of desorption efficiency

45 The desorption efficiencies (DE) of VOCs can vary with the type and batch of sorbent used. Thus it is necessary for each type of sorbent and for each analyte to determine DE over the sample concentration range. This can be done by sampling from a standard atmosphere at appropriate concentration, temperature, humidity etc. Generation of standard atmospheres may not be practicable, and since it is equivalent to measuring effective uptake rate where DE is a hidden variable, it is recommended that DE be measured directly by doping the sorbent of unused blank samplers and treating as for exposed samplers. For doping very small quantities, it may be necessary to use a mixture of components diluted in the elution solvent. Alternatively, in the phase equilibrium method, millilitre amounts of standard solutions are added to unused blank samplers with a pipette and the difference in concentration measured before and about 30 min after addition. With some compounds the phase equilibrium method may give a higher value for DE than direct spiking methods.[25-28]

46 For the 3M 3500 and SKC 575 samplers, inject known amounts of analyte with a microlitre syringe at three or more levels into the samplers through one of the filling ports, seal and leave for at least 16 hr.[29]

47 For the Dräger ORSA 5 sampler, remove one of the porous plugs and inject known amounts of analyte with a microlitre syringe at three or more levels into the sorbent bed. Replace the porous plug and leave for at least 16 hr[30] in the transportation jar.

48 For the Radiello sampler, inject known amounts of analyte onto an unexposed cartridge in its storage tube with a microlitre syringe at three or more levels. Cap and leave for at least 16 hr.

49 DE equals the weight (in µg) recovered divided by the weight (in µg) applied. Plot the DE values against the weight recovered for each sampler load level. If the DE at the load level is less than 0.75 (75%), a sample result corresponding to that level should be discarded (but see paragraph 50).

50 Where mixtures of non-polar analytes are desorbed with pure carbon disulphide, the mutual concentration effect on DE is generally negligible. If the composition of a mixture of polar and non-polar analytes is known approximately, DE values should be established with a similar mixture. It may not be possible to achieve greater than 75% DE for all components of such a mixture with a single desorption solvent. Provided that it can be established that the DE is consistent and that no better solvent can be found, then a compromise is acceptable, although where possible, the taking of a second sample and optimising desorption conditions for both polar and non-polar analytes is preferred.

51 This doping method may not take account of high humidity at the time of sampling. Adsorbed water vapour is a factor which could be simulated by addition of water to the sorbent.

Calibration of uptake rate

52 The uptake rates in Tables 1 and 2 were supplied by the respective manufacturers, except where noted. Evaluations designated level C are a useful guide; however, these rates should be treated as provisional. Where experimental data are not available, it may be necessary to follow the protocol[4] as soon as practicable to determine the relevant uptake rate and its range of applicability.

CALCULATIONS

Mass concentration of analyte

53 Calculate the weight, in µg, of organic vapour in the sample by using the calibration graph prepared for the standard solutions. Also calculate the weights of organic vapour in the blank samplers.

Then:

$$\text{Concentration of organic vapour in air (mg m}^{-3}\text{)} = \frac{1000\,(m - m_{blank})}{DE \times U \times t}$$

where:

m	=	weight (µg) of organic vapour on sample tube
m_{blank}	=	weight (µg) of organic vapour on blank tube
DE	=	desorption efficiency, as read from the DE curve, taking m as the weight recovered
U	=	uptake rate (cm^3 min^{-1})
t	=	exposure time (min)

Note: If it is desired to express concentrations reduced to specified conditions, eg 25°C and 101 kPa, then:

$$C_{corr} = C \times \frac{101}{P} \times \frac{T}{298}$$

where:

P is the actual pressure of the air sampled, in kPa
T is the actual temperature of the air sampled, in Kelvin

Volume concentration of analyte

54 Alternatively, the concentration of organic vapour in the sampled air may be expressed in ppm.

$$\text{Concentration of organic vapour in air (ppm)} = \frac{1000\ (m - m_{blank})}{DE \times U' \times t}$$

where U' = uptake rate (ng ppm^{-1} min^{-1})

55 Uptake rates in cm^3 min^{-1} and ng ppm^{-1} min^{-1} are related by

$$U\ (cm^3\ min^{-1}) = U'\ (ng\ ppm^{-1}\ min^{-1}) \times \frac{24.5}{MW} \times \frac{T}{298} \times \frac{101}{P}$$

where:

24.5 = molar volume (litres) at 298K and 101 kPa
MW = molecular weight of volatile organic compound
T = temperature of sampled air in Kelvin
P = pressure of sampled air in kPa

Note: The definitions of U (SI unit cm^3 min^{-1}) and U' (derived unit ng ppm^{-1} min^{-1}) comply with current ISO and CEN practice, but are the reverse of earlier MDHS definitions.

REPORT

56 It is recommended that the test report should contain the following information:

(a) complete identification of the sample;
(b) reference to this method;
(c) the place and period of sampling;
(d) the barometric pressure and temperature;
(e) the test result;
(f) any unusual features noted during the determination.

ADVICE

Advice on this method and the equipment used can be obtained from the Health and Safety Executive, Health and Safety Laboratory, Broad Lane, Sheffield S3 7HQ, UK (tel 0114 2892000, fax 0114 2892500, email info@hsl.gov.uk).

The Health and Safety Executive wishes where possible to improve the methods described in this series. Any comments that might lead to improvements would therefore be welcome and should be sent to the above address.

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REFERENCES

1 Health and Safety Executive *General COSHH ACOP (Control of Substances Hazardous to Health) and Carcinogens ACOP (Control of Carcinogenic Substances) and Biological Agents ACOP (Control of Biological Agents). Control of Substances Hazardous to Health Regulations 1994: Approved Codes of Practice* (6th edition) HSE Books 1997 ISBN 0 7176 1308 9

2 Health and Safety Executive *Methods for the Determination of Hazardous Substances* MDHS in series HSE Books 1981-97

3 Health and Safety Executive *Analytical quality in workplace air monitoring* MDHS 71 HSE Books 1995 ISBN 0 11 885976 5

4 British Standards Institution *Workplace atmospheres - requirements and test methods for diffusive samplers for the determination of gases and vapours* BS EN 838 1995

5 Health and Safety Executive *Protocol for assessing the performance of a diffusive sampler* MDHS 27 HSE Books 1994 ISBN 0 7176 0635 X

6 Cassinelli M E, DeLon Hull R, Crable J V and Teass A W Protocol for the evaluation of passive monitors *Diffusive sampling: an alternative approach to workplace air monitoring. The proceedings of an international symposium held in Luxembourg, 22-26 September 1986* ed Berlin A, Brown R H and Saunders K J, Royal Society of Chemistry 1987 ISBN 0 85186 343 4

7 Harper M and Guild L V Experience in the use of the NIOSH diffusive sampler evaluation protocol *Am Ind Hyg Assoc J* **57** 1996 1115-23

8 European Committee for Normalisation (CEN) *Workplace atmospheres - general requirements for the performance of procedures for the measurement of chemical agents* EN 482 1994

9 ISO Standard 5725-1976 *Precision of test methods - determination of repeatability and reproducibility for a standard test method by interlaboratory tests*

10 IUPAC Harmonised protocols for the adoption of standardised analytical methods and for the presentation of their performance characteristics *Pure and Appl Chem* 1990 **62** 149-62

11 Pannwitz K-H Measurement of concentrations of the vapours of organic solvents in work areas - Part I *Dräger Review* **56** November 1985 6-29

12 Pannwitz K-H Measurement of concentrations of the vapours of organic solvents in work areas - Part II *Dräger Review* **58** December 1986 9-14

13 Pannwitz K-H Determination of concentrations of the vapours of organic solvents in work areas - Part III *Dräger Review* **61** September 1988 22-25

14 *3M Organic Vapour Monitor sampling and analysis guide* September 1996

15 *SKC Air Sampling Guide 1997* International Edition

16 Cocheo V, Boaretto C and Sacco P High uptake rate radial diffusive sampler suitable for both solvent and thermal desorption *Am Ind Hyg Assoc J* **57** 1996 897-904

17 Lugg G A Diffusion coefficients of some organic and other vapours in air *Anal Chem* **40** 1968 1072-77

18 Fuller E N, Schettler P D and Giddings J C A new method for prediction of binary gas-phase diffusion coefficients *Ind and Eng Chem* **58** 1966 19-27

19 Pannwitz K-H Diffusion coefficients *Dräger Review* **52** January 1984 1-8

20 Feigley C E and Lee B M Determination of sampling rates for organic vapours based on estimated diffusion coefficients *Am Ind Hyg Assoc J* **48** 1987 873-76

21 Feigley C E and Lee B M Determination of sampling rates of passive samplers for organic vapours based on estimated diffusion coefficients *Am Ind Hyg Assoc J* **49** 1988 266-69

22 Hori H and Tanaka I Effect of face velocity on the performance of diffusive samplers *Ann Occ Hyg* **40** 1996 467-76

23 US Occupational Safety and Health Administration *OSHA manual of analytical methods: 07 Organic Vapours* USDOL/OSHA 1989

24 Eller P M and Cassinelli M E *NIOSH manual of analytical methods* 4th edition 1994 US Dept of Health and Human Services Publication 94-113

25 Krajewski J, Gromiec J and Dobecki M Comparison of methods for determination of desorption efficiencies *Am Ind Hyg Assoc J* **41** 1980 531-34

26 Posner J C and Okenfuss J R Desorption of organic analytes from activated carbon, I: Factors affecting the process *Am Ind Hyg Assoc J* **42** 1981 643-46

27 Posner J C Desorption of organic analytes from activated carbon, II: Dealing with the problems *Am Ind Hyg Assoc J* **42** 1981 647-52

28 McCurry J D, Stoll I, Mitchell K M and Zwicki R D Evaluation of desorption efficiency determination methods for acetone *Am Ind Hyg Assoc J* **50** 1989 520-25

29 Rodriguez S T, Gosselink D W and Mullins H E Determination of desorption efficiencies in the 3M 3500 organic vapour monitor *Am Ind Hyg Assoc J* **43** 1982 569-74

30 Mertens H and Beste E Suitability examination of ORSA-5 diffusive samplers made by Drägerwerke AG *Dräger Review* **58** December 1986 22-26

31 Health and Safety Executive *n-Hexane in air: laboratory method using charcoal diffusive samplers, solvent desorption and gas chromatography* MDHS 74 HSE Books 1992 ISBN 0 11 885740 1

32 Mazur J F, Podolak G E, Esposito C G, Rinehart D S and Gleen R E Evaluation of a passive dosimeter for collection of 2-bromo-2-chloro-1,1,1-trifluoroethane and 2-chloro-1,1,2-trifluoroethyl difluoromethyl ether in hospital operating rooms *Am Ind Hyg Assoc J* **41** 1980 317-21

33 Wright M D *Evaluation of the 3M type 3500 monitor for the determination of halothane in air* HSE Internal Report IR/L/AO/85/14 HSL

34 US Occupational Safety and Health Administration *OSHA manual of analytical methods: 49 ethylene oxide* USDOL/OSHA 1989

35 Health and Safety Executive *Mixed hydrocarbons (C_3 to C_{10}) in air* MDHS 60 HSE Books 1992 ISBN 0 11 885998 6

36 Lopes D P DMSO/CS2 mixture: a solvent system for desorption of polar and non-polar paint solvents from activated charcoal *Am Ind Hyg Assoc J* **58** 1997 603-07

37 Health and Safety Executive *Environmental Hygiene Series Guidance Note. Monitoring strategies for toxic substances* EH42 HSE Books 1989 ISBN 0 11 885412 7

38 British Standards Institution *Workplace atmospheres - general requirements for the performance of procedures for the measurement of chemical agents* European Standard BS EN 482 1994 ISBN 0 580 236447

39 Mark D, Robertson A, Gibson H, Borzucki G, Cherrie B and MacLaren W M *Evaluation of diffusive samplers for monitoring toxic gases and vapours in coal mines* Institution of Occupational Medicine report TM/90/11 1990

APPENDIX

Suppliers of charcoal-based organic vapour diffusive samplers that may be suitable for this method and that are available in Europe:

SKC Organic vapour sampler 575	SKC Ltd Unit 11, Sunrise Park Higher Shaftesbury Road Blandford Forum Dorset DT11 8ST 01258 480188
3M Organic vapour monitor 3500/3520	Casella London Ltd Regent House, Wolseley Road Kempston Bedford MK42 7JY 01234 841441
Dräger ORSA-5	Dräger Ltd Kitty Brewster Industrial Estate Blyth Northumberland NE24 4RG 01670 352891
Radiello	Fondazione Clinica del Lavoro - IRCCS Centro di Recerche Ambientali via Tassoni, 6-35125 Padova Italy +39 49 690699
Perkin-Elmer diffusive tube sampler (with charcoal sorbent)	Perkin-Elmer Ltd Post Office Lane Beaconsfield Bucks HP9 1QA 01494 676161

Table 1 Diffusive uptake rates (cm^3 min^{-1}) on Dräger ORSA-5, 3M 3500/20 and SKC 575 samplers (manufacturer-supplied data, except where noted; consult manufacturer for recommended elution solvents and estimated desorption efficiencies)

	Dräger ORSA-5			***3M 3500/20***			***SKC 575-001***	
Compound	*Level*	*Uptake rate*		*Level*	*Uptake rate*		*Level*	*Uptake rate*
Hydrocarbons								
1,3-butadiene	C	7.61			42.8 *(a)*			
n-pentane	C	6.32		B	35.3		A	14.9
1-pentene				C	35.9		C	16.3
2-methylpentane				B	32.0		C	14.1
2-methyl-1,3-butadiene	C	6.51						
n-hexane	B	5.49		A	32.0		B	14.3
n-hexane				A	31.7 *(b)*		B	14.3 *(k)*
n-heptane	B	4.83		B	28.9		B	13.9 *(k)*
1-heptene				C	29.3		C	13.1
n-octane	B	4.62		B	26.6		B	12.7 *(k)*
n-nonane	C	4.32		B	24.6		B	10.6 *(k)*
n-decane	C	4.04		B	23.1		C	10.2
n-dodecane				B	21.5			
cyclopentane				C	36.2			
cyclopentadiene				C	39.5			
dicyclopentadiene				C	23.6		C	11.8
cyclohexane	B	5.58		B	32.4		B	15.6
cyclohexene	B	5.72		B	32.3		C	15.4
methylcyclohexane	C	5.09		B	28.9		B	14.2
trans-1,2-dimethylcyclohexane				C	25.4		C	12.4
4-vinyl-1-cyclohexene				B	27.9			
benzene	A	6.44		B	35.5		A	16.0
toluene	A	5.72		A	31.4		B	14.5
ethylbenzene	B	5.20		C	27.3		B	12.9
m-xylene	B	5.03		B	27.3		B	12.5 *(k)*
o-xylene	B	5.45		B	27.3		B	11.9 *(k)*
p-xylene	B	5.04		B	27.3		B	12.8 *(k)*
styrene	B	5.26		A	28.9		A	13.7 *(c)*
styrene							A	13.7 *(d)*
divinyl benzene				C	23.3			
vinyltoluene				C	25.1		C	12.3 *(c)*
α-methylstyrene	C	4.88		B	25.0		A	12.6 *(c)*
α-methylstyrene							A	12.6 *(d)*
iso-propylbenzene (cumene)	C	5.08		B	24.5		B	12.8
iso-propenylbenzene	C	4.88						
2-ethyltoluene	C	4.78						
3-ethyltoluene	C	4.80						
4-ethyltoluene	C	4.79						
1,2,3-trimethylbenzene	C	4.95		C	24.3		C	12.0
1,2,4-trimethylbenzene	C	4.95		C	24.4		C	12.1
1,3,5-trimethylbenzene	C	4.95		B	26.3		C	12.1
1,2,3,4-tetramethylbenzene							C	11.1
1,2,3,5-tetramethylbenzene							C	11.2
1,2,4,5-tetramethylbenzene							C	11.2
para-t-butyltoluene	C	4.28		B	20.7		B	10.4 *(k)*
naphthalene	C	4.87		C	24.6		C	12.2
α-pinene	C	4.26		C	22.8		A	11.4 *(d)*
β-pinene	C	4.26		C	22.7		B	11.4 *(d)*
Δ^3-carene				C	22.0		B	11.4 *(d)*
limonene	C	4.24		C	21.9		C	11.4 *(d)*
Halocarbons								
methyl chloride	C	9.57			*(g)*			
methyl bromide	C	8.22		C	40.9 *(a)*			
methyl iodide	C	7.24		C	36.7		C	18.7
dichloromethane	B	7.78		A	37.9 *(a)*		A	14.7
chlorobromomethane	C	7.15		B	34.4		C	15.4
chlorotrifluoromethane								
bromoform	C	5.75		C	29.3		C	21.2
chloroform	C	6.66		C	33.5		B	13.0 *(k)*
carbon tetrachloride	C	6.21		C	26.6		B	14.1 *(k)*
carbon tetrabromide				B	30.2			

	Dräger ORSA-5			***3M 3500/20***			***SKC 575-001***		
Compound	*Level*	*Uptake rate*		*Level*	*Uptake rate*		*Level*	*Uptake rate*	
vinyl chloride	B	8.29		B	40.8	*(a)*			
vinyl bromide				C	37.0		C	18.2	
bromoethane		6.95		B	36.4		C	18.1	
1,2-dibromoethane		6.20		B	29.6		C	14.7	
1,1-dichloroethane		6.89		C	33.2				
1,2-dichloroethane	C	6.80		B	33.2		B	14.2	*(k)*
1,1-dichloroethene (vinylidene chloride)	C	6.89		C	35.1		B	12.3	*(k)*
1,2-dichloroethene	C	6.83		B	35.2		A	14.8	
trichloroethene	B	6.56		B	31.1		A	14.9	
1,1,1-trichloroethane	B	5.96		A	30.9		B	14.1	*(k)*
1,1,2-trichloroethane	C	5.94		B	29.7		B	12.5	*(k)*
tetrachloroethene	B	5.98		A	28.3		A	12.9	
1,1,2,2-tetrachloroethane	C	5.42		C	28.4		B	11.8	*(k)*
hexachloroethane	C	4.56		C	26.4		C	11.5	
1-bromobutane	C	5.92							
halothane	B	5.70		C	30.2				
halothane				B	24.0	*(e)*			
halothane				B	23.1	*(f)*			
enflurane	B	5.31		C	28.3		C	13.8	*(c)*
isoflurane	B	5.30		C	28.3		C	13.7	*(c)*
sevoflurane	C	5.03					C	13.1	*(c)*
desflurane							C	14.8	*(c)*
1,1-dichloro-2,2,2-trifluoroethane (R123)				B	30.9				
1,1,1,2-tetrafluoroethane (R134a)				B	37.1				
1,1,2-trichloro-1,2,2-trifluoroethane	C	5.47		C	29.1	*(a)*	C	14.1	
2-chloro-1,1,1,2-tetrafluoroethane (R124)				B	35.8				
1,1,1,2-tetrachloro-2,2-difluoroethane				C	27.5				
1,1,2,2-tetrachloro-1,2-difluoroethane	C	5.11		C	28.2				
1,2-dichloropropane (propylene dichloride)	C	5.73		B	30.6		B	14.3	*(k)*
3-chloropropene (allyl chloride)				C	35.1		C	17.8	
1,2,3-trichloropropane	C	5.16		C	27.4		B	11.9	*(k)*
cis-1,3-dichloropropene				C	30.7		C	15.2	
2-chloro-1,3-butadiene (chloroprene)	C	6.23		C	32.2				
1-chloro-2,3-epoxypropane (epichlorohydrin)	C	6.18		C	29.6		C	16.0	*(c)*
chlorobenzene	B	5.60		B	29.3		C	14.2	
benzyl chloride				C	27.2		C	12.3	
o-dichlorobenzene	C	5.01		B	27.8		C	12.6	
m-dichlorobenzene				C	26.7		C	12.7	
p-dichlorobenzene	C	5.03		B	27.8		C	12.7	
α-chlorotoluene	C	5.35							
o-chlorotoluene				C	27.3		C	12.9	
o-chlorostyrene				C	26.0		A	9.8	*(c,d,k)*
Esters									
methyl formate	C	8.17		C	45.0				
ethyl formate	C	7.32		C	38.8				
methyl acetate	C	7.34		B	37.0				
ethyl acetate	B	6.46		B	34.5		C	15.6	
n-propyl acetate	C	5.76		B	30.1		C	14.6	
iso-propyl acetate	C	5.78		C	31.7		C	14.1	
n-butyl acetate	B	5.04		C	31.6		C	12.7	
iso-butyl acetate	C	4.97		B	31.0		C	12.8	
sec-butyl acetate	C	4.98		B	28.6		C	12.9	
t-butyl acetate	C	5.01		C	29.4		C	12.9	
n-amyl acetate	C	4.58		B	26.0		C	11.8	
iso-amyl acetate	C	4.60		C	27.2		C	11.8	
s-amyl acetate				C	27.2		C	11.9	
1,3-dimethylbutyl acetate (sec-hexyl acetate)				C	25.5		C	11.1	
ethyl hexyl acetate							C	9.8	
ethyl propionate	C	5.42		C	31.2		C	14.0	

	Dräger ORSA-5			3M 3500/20			SKC 575-001		
Compound	*Level*	*Uptake rate*		*Level*	*Uptake rate*		*Level*	*Uptake rate*	
methyl acrylate	C	6.17		C	35.8		A	15.7	*(c)*
ethyl acrylate	C	5.52		C	32.2		B	13.7	*(c,k)*
n-butyl acrylate	C	4.69		C	27.3		B	11.7	*(c,k)*
iso-butyl acrylate							C	12.1	*(c)*
methyl methacrylate	C	5.56		C	31.8		B	13.1	*(c,k)*
ethyl methacrylate				C	29.4		C	13.1	*(c)*
methoxyethyl acetate (methyl cellosolve acetate)	C	5.14		B	29.0		C	13.1	
2-ethoxyethyl acetate (cellosolve acetate)	C	4.57		B	26.6		C	12.0	
1-methoxy-2-propyl acetate (propylene glycol monomethyl ether acetate)	C	5.26		B	25.2		C	12.2	
2-methoxy-1-propyl acetate							C	12.0	
2-butoxyethyl acetate (butyl cellosolve acetate)	C	4.39		B	24.3		C	10.5	
vinyl acetate	C	6.20		C	35.8	*(i)*			
benzyl acetate				C	22.6		C	11.3	
Alcohols and glycol ethers									
ethanol	C	8.91		B	43.7		C	20.9	*(c)*
2-chloroethanol (ethylene chlorohydrin)	C	6.68		C	33.9				
n-propanol	C	7.44		B	39.7		C	18.5	*(c)*
iso-propanol	B			A	39.4		C	17.8	*(c)*
2-propen-1-ol (allyl alcohol)	C	7.66		C	40.4		C	18.4	*(c)*
n-butanol	B	6.46		B	34.3		C	15.5	*(c)*
iso-butanol	B	6.08		B	35.9		C	15.6	*(c)*
sec-butanol	B	6.73		C	34.8		C	15.6	*(c)*
t-butanol	C	6.55		C	35.8		C	15.8	*(c)*
n-amyl alcohol				B	31.2		C	13.9	*(c)*
iso-amyl alcohol	C	5.46		B	32.3		C	13.9	*(c)*
sec-amyl alcohol				C	31.2				
hexyl alcohol				C	28.5		C	12.6	
methyl amyl alcohol (methyl isobutyl carbinol)				C	29.2		C	12.8	*(c)*
2-ethyl hexanol	C	4.38		C	25.2		C	10.9	
iso-octyl alcohol	C	4.32		C	25.1		C	11.1	
nonyl alcohol				C	23.8		C	10.2	
decyl alcohol				C	22.7		C	9.6	
dodecyl alcohol				C	20.8		C	8.7	
2-methoxyethanol	C	6.34		B	36.3		C	16.1	*(c)*
2-ethoxyethanol	C	5.91		B	32.4		C	14.4	
iso-propoxyethanol				C	29.5				
2-methoxy-1-propanol							C	14.4	*(c)*
1-methoxy-2-propanol (propylene glycol monomethyl ether)	B	5.72		B	32.4		C	14.5	*(c)*
2-butoxyethanol	B	4.76		B	28.2		C	12.0	*(c)*
2,3-epoxy-1-propanol (glycidol)				C	37.1		C	16.7	*(c)*
ethylene glycol				C	24.3		C	17.4	*(c)*
ethylene glycol monohexyl ether							C	10.5	
dipropylene glycol methyl ether	C	4.25		C	25.3		C	10.8	*(c)*
cyclohexanol	C	5.11		B	29.5		C	13.5	
methyl cyclohexanol				C	25.3		C	12.5	*(c)*
benzene-1,3-diol (resorcinol)				C	25.8				
terpineol				C	20.0		C	10.5	*(d)*
furfuryl alcohol				C	30.6				
diacetone alcohol	C	5.05		B	28.2		C	12.4	*(c)*
Ketones									
acetone	B	7.87		B	40.1	*(i)*	A	15.2	*(c)*
2-butanone	C	6.77		A	36.3	*(i)*	B	17.1	*(c,k)*
2-pentanone	C	5.95		B	33.0		B	15.7	*(c)*
3-pentanone (diethylketone)				C	32.7		C	14.8	*(c)*
methyl isopropyl ketone				C	32.8		C	14.8	*(c)*
2-hexanone	C	7.10		B	29.7	*(i)*	C	13.4	*(c)*

	Dräger ORSA-5			*3M 3500/20*			*SKC 575-001*		
Compound	*Level*	*Uptake rate*		*Level*	*Uptake rate*		*Level*	*Uptake rate*	
3-heptanone (ethyl butyl ketone)				C	28.0		C	12.3	*(c)*
4-heptanone (dipropyl ketone)				C	27.8		C	12.3	*(c)*
5-methyl-2-hexanone	C	4.92							
diisobutyl ketone	C	4.24		B	24.6		B	10.3	*(c,k)*
2,6-dimethylheptan-4-one	C	4.24					C	10.7	*(c)*
4-methylpentan-2-one (MIBK)	B	5.27		B	30.0		B	13.5	*(c)*
4-methylpentan-3-ene-2-one (mesityl oxide)	C	5.70		B	31.2		C	13.7	
methyl n-amyl ketone (2-heptanone)	C	4.82		C	27.9		C	12.2	*(c)*
methyl isoamyl ketone				C	28.0		C	12.2	*(c)*
ethyl amyl ketone (5-methyl-3-heptanone)				C	26.4		C	11.4	*(c)*
2,4-pentanedione				C	31.7				
butyrolactone				C	33.7		C	15.8	*(c)*
cyclohexanone	C	6.02		B	28.9		B	15.1	*(d)*
isophorone	C	4.51		B	21.7		C	11.3	*(c)*
Ethers									
diethyl ether	C	6.89		C	26.8		C	16.3	
diisopropyl ether	C	5.12		C	31.2		C	13.2	
dichloroethyl ether	C	5.21		C	26.1		C	12.7	
1-dichloro-2-difluoroethyl ether	C	5.23							
1,4-dioxane	C	6.90		C	34.5		C	16.0	*(c)*
dimethoxymethane	C	6.65		C	37.9		C	17.1	
tetrahydrofuran	C	7.00		C	37.2		C	17.4	*(c)*
iso-propyl glycidyl ether				C	29.1		C	12.8	
butyl glycidyl ether				C	27.0		C	11.6	
phenyl glycidyl ether				C	22.2		C	11.1	
methyl t-butyl ether				A	30.8		A	13.6	
ethyl t-butyl ether				C	29.9		B	13.1	*(k)*
methyl t-amyl ether				C	29.6		B	13.1	*(k)*
diphenyl ether	C	3.93		C	31.2		C	10.4	
Miscellaneous									
acetonitrile	C	8.86		C	48.2		C	22.4	*(c)*
acrylonitrile	C	7.94		C	43.8		C	19.7	
camphor	C	4.10		C	21.4		C	10.8	*(c)*
carbon disulphide	B	7.60		C	42.8				
ethyl mercaptan				C	41.1				
ethylene oxide	C	8.96		B	49.3	*(h)*			
propylene oxide	C	7.42		B	37.7	*(a)*	C	19.9	
furfural				C	34.3				
morpholine				C	33.1				
N,N-dimethylaniline							C	12.0	
dimethyl formamide				C	35.5		C	16.4	*(c)*
dimethyl acetamide				C	32.0				
pyridine	C	6.44		C	34.9		C	16.3	
N-methyl-2-pyrrolidone				C	28.8				
1,1-dichloronitroethane				C	28.5				

Notes

a 3M 3520 sampler with back-up section.
b MDHS 74 (reference 31).
c SKC 575-002 sampler with Anasorb® 747. For the majority of compounds with an entry for the 575-001 sampler, the Anasorb® 747 type can also substitute for the 575-001 sampler with the same uptake rates.
d SKC 575-003 sampler with Anasorb® 727.
e Re-calculated from data of Mazur et al, 1980 (reference 32).
f HSE Internal Report, 1985 (reference 33).
g 3M OVM not recommended for methanol or methyl chloride.
h 3M 3550 ethylene oxide monitor (reference 34).
i Refrigerate and analyse as quickly as possible if sampled under high humidity.
k SKC bi-level validation (reference 7).

Evaluation levels A-C are designated as follows (see also paragraphs 11-12):
A: Full (EN 838 level 1A or NIOSH protocol or close equivalent);

B: Partial (EN 838 level 1B, or other tests in which experimental uptake rates were measured over a more limited range than that specified by level 1A or 1B, as described in EN 482:1994);

C: Theoretical or ideal uptake rates calculated from known or estimated diffusion coefficients and a geometric constant characteristic of the sampling device.

Table 2 Diffusive uptake rates (cm^3 min^{-1}) on the Radiello sampler (manufacturer-supplied data)

		Radiello	
Compound	*Level*	*Uptake rate*	*(a)*
Hydrocarbons			
n-pentane	A	74	
n-hexane	A	66	
cyclohexane	A	47	
n-heptane	A	58	
n-octane	A	53	
2,2,4-trimethylpentane (isooctane)	A	55	
n-decane	A	43	
benzene	A	80	
toluene	A	74	
xylene isomers	A	61	
styrene	A	61	
isopropylbenzene (cumene)	A	58	
Halocarbons			
dichloromethane	B	90	*(b)*
bromochloromethane	B	70	
1,1,1-trichloroethane	A	47	
trichloroethene	A	65	
tetrachloroethene	A	65	
1,2-dichloropropane	A	66	
Esters			
Ethyl acetate	A	64	
n-butyl acetate	A	60	
isobutyl acetate	A	63	
methyl methacrylate	B	68	
Alcohols and glycol ethers			
iso-propanol	A	52	*(c)*
iso-butanol	A	77	
n-butanol	A	74	
2-ethoxyethanol	A	55	*(c)*
2-butoxyethanol	A	56	*(c)*
1-methoxy-2-propanol	A	55	*(c)*
1-ethoxy-2-propanol	A	68	*(c)*
2-methoxyethyl acetate	A	64	
2-ethoxyethyl acetate	A	54	
2-butoxyethyl acetate	A	41	
1-methoxy-2-propyl acetate	A	60	
Ketones			
acetone	A	77	*(c,d)*
2-butanone (MEK)	A	57	
4-methylpentan-2-one (MIBK)	A	64	
cyclohexanone	A	60	*(c)*
Ethers			
methyl t-butyl ether	B	65	
ethyl t-butyl ether	B	61	
Miscellaneous			
acrylonitrile	B	75	

Notes

a Uptake rates include allowance for desorption efficiency.

b 8-hr exposure was at 1/3 of ACGIH limit value.

c If exosure was prolonged at >60% RH add water to standards to match water content of charcoal desorbate.

d If not exposed for more than 6 hr at limit value.

Table 3 Retention indices of selected VOCs on BP-1 and BP-10 phases

	BP-1		*BP-10*
propane	300	propane	300
dichlorodifluoromethane (R12)	311	dichlorodifluoromethane (R12)	318
methyl chloride	348	1,2-dichloro-1,1,2,2-tetrafluoroethane (R114)	353
1,2-dichloro-1,1,2,2-tetrafluoroethane (R114)	359	isobutane	359
isobutane	364	butane	400
methanol	370	methyl chloride	402
chloroethene (vinyl chloride)	378	chloroethene (vinyl chloride)	420
butane	400	2-methylbutane	478
methyl bromide	421	methyl bromide	482
ethyl chloride	434	ethyl chloride	492
ethanol	450	methanol	500
acetonitrile	470	pentane	500
trichlorofluoromethane (R11)	482	trichlorofluoromethane (R11)	503
enflurane	486	2,2-dimethylbutane	528
acetone	487	1,1,2-trichloro-1,2,2-trifluoroethane	528
2-methylbutane	488	dichlorofluoromethane (R21)	532
iso-propanol	488	dimethylethanolamine	553
dichlorofluoromethane (R21)	491	propylene oxide	553
pentane	500	1,1-dichloroethene (vinylidene chloride)	555
dimethoxymethane	511	ethanol	559
methyl acetate	511	2-methylpentane	561
1,1-dichloroethene (vinylidene chloride)	513	2,3-dimethylbutane	561
dichloromethane	514	3-methylpentane	582
1,1,2-trichloro-1,2,2-trifluoroethane (R113)	524	acetone	589
2,2-dimethylbutane	532	n-hexane	600
n-propanol	539	iso-propanol	601
halothane	541	methyl acetate	603
vinyl acetate	560	enflurane	607
cyclopentane	562	dichloromethane	608
2-methylpentane	563	acetonitrile	637
2,3-dimethylbutane	563	methylcyclopentane	642
2-butanone	571	halothane	644
3-methylpentane	579	vinyl acetate	644
cis-1,2-dichloroethene	592	2-methylhexane	662
ethyl acetate	596	n-propanol	665
chloroform	600	2,3 -dimethylpentane	669
n-hexane	600	3-methylhexane	673
iso-butanol	610	cyclohexane	676
methoxyethanol	616	ethyl acetate	685
1,2-dichloroethane	627	cis-1,2-dichloroethene	685
methylcyclopentane	627	2,2,4-trimethylpentane	687
1,1,1-trichloroethane	634	methyl acrylate	690
n-butanol	643	2-butanone	693
iso-propyl acetate	643	1,1,1-trichloroethane	693
benzene	652	carbon tetrachloride	697
1-methoxy-2-propanol (PGME)	658	chloroform	700
cyclohexane	662	n-heptane	700
carbon tetrachloride	663	cyclohexene	712
2-methylhexane	664	benzene	723
2,3-dimethylpentane	668	iso-propyl acetate	727
3-methylhexane	674	iso-butanol	739
cyclohexene	678	2,4-dimethylhexane	736
1,2-dichloropropane	684	methylcyclohexane	736
tert-butyl acetate	687	1,2-dichloroethane	745
2,2,4-trimethylpentane	691	methoxyethanol	755
trichloroethene	691	trichloroethene	755
ethoxyethanol	695	tert-butyl acetate	763
n-propyl acetate	695	2-methylheptane	768
methyl methacrylate	696	1-methoxy-2-propanol	773
n-heptane	700	3-methylheptane	774
methoxyflurane	706	n-butanol	777
cis-1,2,dichloropropene	720	1,2-dichloropropane	778
methylisobutylketone	723	methyl methacrylate	782

	BP-1		*BP-10*
methylcyclohexane	728	n-propyl acetate	784
2,4-dimethylhexane	735	n-octane	800
1-ethoxy-2-propanol	738	methoxyflurane	806
trans-1,2-dichloropropene	739	2,4-dimethylheptane	820
sec-butyl acetate	745	ethoxyethanol	820
1,1,2-trichloroethane	747	cis-1,2-dichloropropene	821
2-ethoxy-1-propanol	754	sec-butyl acetate	823
iso-butyl acetate	757	toluene	825
toluene	761	methylisobutyl ketone	831
2-methylheptane	765	iso-butyl acetate	840
hexanal	777	1-ethoxy-2-propanol	843
diethyleneglycol diethyl ether	783	tetrachloroethene	846
1,2-dibromoethane	787	diethylene glycol diethyl ether	854
propoxyethanol	790	trans-1,2-dichloropropene	862
n-butyl acetate	795	3-methyloctane	872
n-octane	800	1,1,2-trichloroethane	876
furfural	803	n-butyl acetate	883
methoxyethyl acetate	807	hexanal	891
tetrachloroethene	807	n-nonane	900
2,4-dimethylheptane	824	di-n-butyl ether	905
furfuryl alcohol	830	1,2-dibromoethane	905
chlorobenzene	837	propoxyethanol	913
diacetone alcohol	842	ethylbenzene	922
1-methoxy-2-propyl acetate	843	chlorobenzene	922
ethylbenzene	855	p-xylene	929
amyl acetate	859	m-xylene	929
p-xylene	864	methoxyethyl acetate	940
m-xylene	864	amyl acetate isomer	948
4-methyloctane	865	amyl acetate isomer	951
allyl glycidyl ether	868	o-xylene	960
cyclohexanone	871	α-pinene	962
3-methyloctane	873	styrene	968
tetrahydrofurfuryl alcohol	874	iso-propylbenzene (cumene)	983
ehoxyethyl acetate	876	furfural	987
styrene	881	allyl glycidyl ether	999
1,1,2,2-tetrachloroethane	886	n-decane	1000
o-xylene	887	ethoxyethyl acetate	1002
butoxyethanol	890	N-methyl-2-pyrrolidone	1009
n-nonane	900	cyclohexanol	1010
iso-propylbenzene	919	n-propylbenzene	1014
bromobenzene	921	butoxyethanol	1015
ethanediol monoacetate	925	furfuryl alcohol	1019
2-methylcyclohexanone	930	m-ethyltoluene	1022
3-methylcyclohexanone	931	furfuryl alcohol	1023
4-methylcyclohexanone	937	p-ethyltoluene	1023
benzaldehyde	940	1,3,5-trimethylbenzene	1029
α-pinene	941	cyclohexanone	1030
n-propylbenzene	949	1,1,2,2-tetrachloroethane	1045
phenol	951	ethanediol monoacetate	1046
m-ethyltoluene	956	o-ethyltoluene	1047
p-ethyltoluene	958	α-methylstyrene	1050
1,3,5-trimethylbenzene	963	2-methylcyclohexanone	1060
3-methylnonane	972	1,2,4-trimethylbenzene	1060
α-methylstyrene	972	3-methylcyclohexanone	1088
o-ethyltoluene	975	4-methylcyclohexanone	1095
1,2,4-trimethylbenzene	990	1,2,3-trimethylbenzene	1097
benzyl chloride	997	p-dichlorobenzene	1099
n-decane	1000	n-undecane	1100
p-dichlorobenzene	1004	1-methyl-2-isopropylbenzene	1104
N-methyl-2-pyrrolidone	1009	benzaldehyde	1105
1,2,3-trimethylbenzene	1019	1,3-diethylbenzene	1111
o-dichlorobenzene	1027	indane	1117
o-cresol	1027	propenylbenzene	1117
indane	1033	1,4-diethylbenzene	1118
1-methyl-2-iso-propylbenzene	1034	n-butylbenzene	1120
indene	1039	benzyl chloride	1128
propenylbenzene	1041	ethanediol diacetate	1130

	BP-1		*BP-10*
p-cresol	1047	o-dichlororobenzene	1135
m-cresol	1047	1,3 dimethyl-4-ethylbenzene	1146
1,4-diethylbenzene	1051	indene	1147
n-butylbenzene	1052	benzyl chloride	1162
butoxyethyl acetate	1061	butoxyethyl acetate	1185
1,3-dimethyl-4-ethylbenzene	1075	n-dodecane	1200
vinyl pyrrolidone	1077	phenol	1222
nonanal	1085	1,1,2,3,4,4-hexachloro-1,3-butadiene	1270
2,6-xylenol	1093	o-cresol	1274
n-undecane	1100	2,6-xylenol	1296
isophorone	1113	tridecane	1300
2,4-xylenol	1127	ethylhexyl methacrylate	1308
2,5-xylenol	1127	isophorone	1308
decanal	1129	p-cresol	1311
3,5-xylenol	1144	m-cresol	1311
2,3-xylenol	1158	vinyl pyrrolidone	1322
3,4-xylenol	1171	naphthalene	1328
2-(isopropyl)phenol	1175	2,4-xylenol	1360
naphthalene	1196	2,5-xylenol	1360
n-dodecane	1200	2,3-xylenol	1400
ethylhexyl acrylate	1215	3,5-xylenol	1400
1,1,2,3,4,4-hexachloro-1,3-butadiene	1223	n-tetradecane	1400
n-tridecane	1300	tetrahydrofurfuryl methacrylate	1400
2-methylnaphthalene	1310	3,4-xylenol	1434
1-methylnaphthalene	1328	2-methylnaphthalene	1447
2,6-bis(isopropyl)phenol	1346	1-methylnaphthalene	1470
biphenyl	1388	n-pentadecane	1500
n-tetradecane	1400	2,6-bis(iso-propyl)phenol	1524
n-pentadecane	1500	biphenyl	1538
n-hexadecane	1600	n-hexadecane	1600

Notes

1 Retention index data for selected VOCs in Table 3 were compiled from HSL in-house sources. The majority of compounds listed in Table 1 (manufacturer sources) are found here, but no exact correspondence of the two lists is implied.

2 GC retention indices based on the n-alkanes indicate the order of elution, but the absolute values are not intended to be definitive. Most were measured using the GC conditions in paragraph 40. Interpolated values are affected by temperature programming rates and other factors. They are normally reproduced to within ± 5 units with equivalent phases and similar conditions.

3 More retention indices of 150 gasoline hydrocarbons on OV1701, equivalent to BP-10, are listed in MDHS 60 (reference 35).

TITLES IN THE MDHS SERIES

1 Acrylonitrile *charcoal tube/gas chromatography (GC)*
2 Acrylonitrile *pumped thermal desorption/GC*
3 Standard atmospheres *syringe injection*
4 Standard atmospheres *permeation tube*
5 On-site validation of methods
6/2 Lead *atomic absorption (AA)*
7 Lead *X-ray fluorescence (XRF)*
8 Lead *colorimetric (dithizone)*
9 Tetra alkyl lead *personal monitoring*
10/2 Cadmium *AA*
11 Cadmium *XRF*
12/2 Chromium *AA*
13 Chromium *XRF*
14 Total inhalable and respirable dust *gravimetric*
15 Carbon disulphide *charcoal tube/GC*
16 Mercury *adsorbent tube (Hydrar) AA*
17 Benzene *charcoal tube/GC*
18 Tetra alkyl lead *continuous monitoring*
19 Formaldehyde *colorimetric (Chromotropic acid)*
20 Styrene *pumped charcoal tube/GC*
21 Glycol ethers *charcoal tube/GC*
22 Benzene *thermal desorption/GC*
23 Glycol ethers *thermal desorption/GC*
24 Vinyl chloride *charcoal tube/GC*
25/2 Organic isocyanates *reagent bubbler/HPLC*
26 Ethylene oxide *charcoal tube/GC*
27 Diffusive sampler evaluation protocol
28 Chlorinated hydrocarbons *charcoal tube/GC*
29/2 Beryllium *AA*
30/2 Cobalt *AA*
31 Styrene *pumped thermal desorption/GC*
32 Phthalate esters *solvent desorption/GC*
33 Adsorbent tube standards
34 Arsine *colorimetric (diethyldithiocarbamate)*
35 HF and fluorides *ion-selective electrode*
36 Toluene *charcoal tube/GC*
37 Quartz in respirable airborne dust *direct infra-red*
38 Quartz in respirable airborne dust *KBr disc technique*
39/4 Asbestos fibres *light microscopy (European reference version)*
40 Toluene *thermal desorption/GC*
41/2 Arsenic *AA*
42/2 Nickel *AA*
43 Styrene *diffusive/thermal desorption/GC*
44 Styrene *diffusive/solvent desorption/GC*
45 Ethylene dibromide *solvent desorption/GC*
46 Platinum *AA*
47 Rubber fume in air measured as total particulates and cyclohexane soluble material
48 Newspaper print rooms: measurements of total particulates and cyclohexane soluble material in air
49 Aromatic isocyanates *acid hydrolysis/ diazotisation*
50 Benzene *diffusive/thermal desorption/GC*
51/2 Quartz in respirable dusts *X-ray diffraction (direct method)*
52/2 Hexavalent chromium in chromium plating mists *colorimetric (1,5-diphenylcarbazide)*
53 1,3 Butadiene *thermal desorption/GC*
54 Protocol for assessing the performance of a pumped sampler for gases and vapours
55 Acrylonitrile *diffusive/thermal desorption/GC*
56/2 Hydrogen cyanide *ion-selective electrode*
57 Acrylamide *liquid chromatography*
58 Mercury vapour
59 Manmade mineral fibres
60 Mixed hydrocarbons
61 Total hexavalent chromium compounds in air *colorimetric*
62 Aromatic carboxylic acid anhydrides
63 Butadiene *diffusive/thermal desorption/GC*
64 Toluene *charcoal diffusive/solvent desorption/GC*
65 Mine road dust: determination of incombustible matter
66 Mixed hydrocarbons (C_5 to C_{10}) in air *diffusive/ thermal desorption/GC*
67 Total (and speciated) chromium in chromium plating mists *colorimetric (1,5-diphenylcarbazide)*
68 Coal tar pitch volatiles
69 Toluene *diffusive/solvent desorption/GC*
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76 Cristobalite in respirable dusts *X-ray diffraction (direct method)*
77 Asbestos in bulk materials
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80 Volatile organic compounds *diffusive/thermal desorption/GC*
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85 Triglycidyl isocyanurate in air *pumped filter/ desorption/liquid chromatography*
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