MDHS

Methods for the Determination of
Hazardous Substances
Health and Safety Laboratory

HSE
Health & Safety
Executive

96

Volatile organic compounds in air (4)

Laboratory method using pumped solid sorbent tubes, solvent desorption and gas chromatography

March 2000

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 damage their health 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 people who could 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.

2 Guidance is given in the Approved Codes of Practice for the Control of Substances Hazardous to Health Regulations, the *General COSHH ACOP*, and the Control of Carcinogenic Substances Regulations, the *Carcinogens ACOP*, which are included in a single publication with the COSHH Regulations.[2]

Occurrence, properties and uses

3 Occurrence, properties and uses of many volatile organic compounds (VOCs) are summarised in HSE's Guidance Note EH64[3] *Summary criteria for occupational exposure limits*. Some are covered more fully in EH65[4] *Criteria document for an occupational exposure limit* or EH72[5] *Risk assessment document*. See Table 1 for relevant Guidance Notes for specific compounds.

Note 1: *No specific meaning is intended for VOCs. The definition includes all organic compounds of medium volatility, in a boiling point range of approximately 0-400°C or vapour pressures in the range 0.10-100 kPa. Paragraph 12 indicates compound classes within this broad definition for which this method is appropriate.*

Health effects

4 The health effects of many VOCs are summarised in EH64[3] *Summary criteria for occupational exposure limits*. Some are covered more fully in EH65[4] *Criteria document for an occupational exposure limit*, EH72[5] *Risk assessment document*, or Toxicity Reviews.[6] See Table 1 for relevant Guidance Notes and Toxicity Reviews for specific compounds.

Health and safety precautions

5 Prevention and control of exposure, emergency procedures and health surveillance are described more fully in HSE publications on COSHH.[7,8,9,10,11]

6 VOCs are typically solvents, used principally for cleaning or degreasing, or for dissolving another component (eg a paint or adhesive), or they may be chemical intermediates in their own right. Workers may be exposed wherever VOCs are manufactured, stored, used or disposed of, but they are most likely to be exposed when:

- vapour arises from the handling of solvent in the liquid phase;
- vapour is formed from a fugitive escape;
- vapour is produced by a drying film.

Exposure limits

7 Regulation 7 of the Control of Substances Hazardous to Health Regulations 1999[1,2] lays down the requirements for using maximum exposure limits (MELs) and occupational exposure standards (OESs) for achieving adequate control of worker exposure. MELs are published in EH40[12] Table 1, and OESs in Table 2. The criteria on which the limits are based are documented in EH64[3] and EH 65.[4]

8 The Health and Safety Commission has approved an OES or an MEL, 8-hour time-weighted average (TWA) and/or short-term (15-minute) exposure limit for some VOCs. See Table 1 for relevant OELs for specific compounds.

Analytical methods

9 There may be alternative methods available for the determination of a particular analyte. With the exception of a few cases, where an exposure limit is linked to a specific method (eg rubber fume or asbestos), the use of methods not included in the MDHS series[13] is acceptable, provided that they have been shown to have the accuracy and reliability appropriate to the application.

10 Within this MDHS series,[13] there are three other general methods for volatile organic compounds. The first,[14] MDHS72, is a laboratory method using pumped solid sorbent tubes, thermal desorption and gas chromatography. The second,[15] MDHS80, is a laboratory method using diffusive solid sorbent tubes, thermal desorption and gas chromatography. The third,[16] MDHS88, is a laboratory method using diffusive samplers, solvent desorption and gas chromatography. MDHS72 includes and replaces MDHS2 (acrylonitrile), MDHS22 (benzene), MDHS23 (glycol ethers), MDHS31 (styrene), MDHS40 (toluene), MDHS53 (butadiene) and MDHS60 (mixed hydrocarbons). MDHS80 includes and replaces MDHS43 (styrene), MDHS50 (benzene), MDHS55 (acrylonitrile), MDHS63 (butadiene) and MDHS66 (mixed hydrocarbons). MDHS88 includes and replaces MDHS44 (styrene), MDHS64 and 69 (toluene), and MDHS74 (hexane). This MDHS includes and replaces MDHS1 (acrylonitrile), MDHS15 (carbon disulphide), MDHS17 (benzene), MDHS20 (styrene), MDHS21 (glycol ethers), MDHS24 (vinyl chloride), MDHS26 (ethylene oxide), MDHS28 (chlorinated hydrocarbons), MDHS32 (dioctyl phthalate), MDHS36 (toluene) and MDHS45 (ethylene dibromide). There may also be some alternative MDHS methods for specific compounds, for example diethyl sulphate and dimethylsulphate (MDHS89).

PRINCIPLE

11 A measured volume of sample air is drawn through one (or more) sorbent tubes in series. An appropriate sorbent (or sorbents) is selected for the compound or mixture to be sampled. Provided suitable sorbents are chosen and the breakthrough volume is not exceeded, volatile organic components are fully retained by the sorbent tube and thus are removed from the flowing air stream. 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

12 The method described is for pumped tubes containing a sorbent and used for the determination of the time-weighted average concentrations of VOCs in workplace atmospheres. It is appropriate for a wide range of VOCs, including hydrocarbons, halogenated hydrocarbons, ester, glycol ethers, ketones and alcohols. A number of sorbents are recommended for the sampling of these VOCs, each sorbent having a different range of applicability. However, activated coconut shell charcoal is frequently used. Very polar compounds may require derivatisation; very low boiling compounds will only be partially retained by the sorbents and can only be estimated qualitatively. Semi-volatile compounds will be fully retained by the sorbents, but may only be partially recovered.

Note 2: *The sorbents listed in Appendix 1 and elsewhere in this MDHS are those known to perform as described. Each sorbent that is identified by a trade marked name is unique and has a sole manufacturer; however, they are widely available from many different suppliers.*

13 The sorbent tubes described here are supplied pre-packed and ready to use. Validation data are available principally from US regulatory authorities, ie NIOSH[17] and OSHA.[18] Manufacturers' products are generally equivalent, although there may be some batch-to-batch variation in coconut shell charcoal (see paragraphs 38-40).

14 The method is generally valid for the measurement of airborne VOC vapour in the concentration range of approximately 1-1000 mg/m^3 of VOCs for a 10 l sample size. The upper limit of the range 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.

15 HSG173[19] advises employers about how they should conduct investigations into the nature, extent and control of exposure to 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 are for personal sampling in the breathing zone and result in a TWA value of the concentration. The method may also, however, be used for background or fixed location sampling. Alternative on-site procedures, such as portable gas chromatography, infra-red spectrophotometry or a total organic analyser, should be used to monitor rapidly changing concentrations of single substances or mixtures.

SAMPLING EQUIPMENT

Sorbent tube

16 A sampling tube, typically consisting of a glass tube with both ends flame-sealed, 70 mm long with an outside diameter of 6 mm and an inside diameter of 4 mm, containing two sections of sorbent. In the case of charcoal, the sorbing section usually contains 100 mg of charcoal and the back-up section 50 mg. The sections are separated and their contents are held in place with an inert material, eg glass wool plugs (preferably silanised). Glass tubes should be held in protective holders to prevent breakage.

17 Sorbents other than charcoal may be used for certain applications. A description of sorbent types is given in Appendix 1. Recommended sorbents and appropriate tube sizes for particular VOCs are given in Tables 2 and 3. Equivalent sorbents may be used.

18 Instead of commercial two-section tubes, two single-section tubes in series may be used. This arrangement has the advantage that it is not necessary to store tubes at sub-ambient temperatures after sampling, to prevent migration of the sorbed compounds from one section to the other.

19 Tubes meeting these requirements are commercially available; however, the user can make them. Metal tubes may also be used with appropriate end caps. Self-packed samplers should not be used unless they can be shown to have reproducible and constant sorption properties.

20 Polyurethane plugs may be used in place of silanised glass wool; however, they are known to sorb certain pesticides[20] for which this MDHS is inapplicable.

21 When it is desirable to sample highly volatile compounds for extended periods, or at a high-volume flow rate, a larger sampling device can be used, provided the proportions of the tube and its charcoal contents are scaled similarly to the base dimensions, to provide nominally the same linear flow rate and contact time with the charcoal bed.

Polyethylene end caps

22 Custom-made to fit snugly over the sorbent tubes (paragraph 16) to prevent leakage.

Sampling pumps

23 Sampling pumps, complying with the provisions of BS EN 1232,[21] with an adjustable flow rate, incorporating a flowmeter or a flow fault indicator, capable of maintaining the selected flow rate to within ±5% of the nominal value throughout the sampling period, and which people can wear without impeding their normal work activity.

Flowmeter

24 Flowmeter, portable, capable of measuring the appropriate flow rate to within ±5%, and calibrated against a primary standard.[22] Flowmeters incorporated in sampling pumps are not suitable for accurate measurement of the flow rate. However, they can be useful for monitoring the performance of samplers, provided they are sensitive enough.

Tubing

25 Plastic or rubber tubing about 90 cm long of appropriate diameter to ensure a leak-proof fit to both pump and sample tube or tube holder, if used. Clips should be provided to hold the sorbent tube and connecting tubing to the wearer's lapel area. It is not recommended to use tubes with any tubing upstream of the sorbent as sample losses may occur.

LABORATORY APPARATUS

Glassware

26 A selection of laboratory glassware, including volumetric flasks complying with the requirements of BS 1792.[23]

Disposable gloves

27 Disposable gloves, impermeable, to avoid the possibility of contamination from the hands and to protect them from contact with harmful substances. Vinyl or nitrile gloves are suitable.

Balance

28 A balance, calibrated against a primary standard, for the preparation of the internal standard solution and calibration standards. The balance should be capable of weighing to ±0.01 mg over the range 0-100 mg.

Micropipettes

29 A set of adjustable positive displacement micropipettes, calibrated against a primary standard, for the preparation of calibration and sample solutions.[24]

Gas chromatograph

30 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 3: *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

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

Integrator

32 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.

REAGENTS

33 During the analysis, use only reagents of a recognised analytical grade.

Note 4: *Safety precautions: carbon disulphide vapour is toxic. Exposure by all routes should be avoided. Usage should be restricted to a well-ventilated hood. Carbon disulphide is highly flammable. Many of the compounds to be analysed are also toxic, eg benzene; see HSE Guidance Notes for more information. Exposure by all routes should be avoided, eg during the preparation of standard solutions.*

Calibrants

34 Most analytes listed in Tables 2-3 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. 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

35 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) is commercially available. Carbon disulphide is normally recommended for the desorption of non-polar compounds from activated carbon.

36 For polar compounds and mixtures of polar and non-polar compounds there is no ideal universal desorption solvent. Dichloromethane, methanol, higher alcohols, dimethylformamide and acetonitrile have been used as eluants, either singly or mixed with each other or carbon disuphide. Tables 2 and 3 give examples of suitable desorption solvents other than pure carbon disulphide.

37 The use of carbon disulphide desorption solvent can result in problems when polar analytes are collected from humid atmospheres. Polar analytes may be soluble in a water phase which forms following desorption with carbon disulphide when sufficient water is collected with the sample. A desorption solvent modifier should be present at a sufficient concentration to result in a homogeneous solution in desorbed samples. Dimethylformamide may be suitable for this purpose.

Sorbents

38 Normally, charcoal is used as the collection medium. A particle size of 0.35-0.85 mm is recommended. Before packing the tubes, the charcoal should be heated in an inert atmosphere, eg high-purity nitrogen, at approximately 600°C for 1 hour. To prevent recontamination of the charcoal, it should be kept in a clean atmosphere during cooling to room temperature, storage, and loading into the tubes. Tubes prepacked by the manufacturer with pre-conditioned charcoal are also available and require no further conditioning.

39 Activated charcoal is usually processed from coconut shells. For some applications, petroleum-based charcoal is preferred (see Table 1). Some methods or manufacturers recommend synthetic carbons as alternatives to charcoal of biological origin.

40 The sorptive capacity and desorption efficiency of different batches of activated charcoal may vary. Commercial tubes, if used, should be purchased from the same batch and in sufficient number to provide consistent performance for a definite period of time.

41 Sorbents other than charcoal may be used for certain applications (see paragraph 17).

SAMPLING

Sampling procedure

42 Select a sampler appropriate for the compound or mixture to be sampled. Published methods giving further information on sampling and analysis details for specific VOCs are referenced in Tables 2 and 3. The source references give details of suitable flow rates and recommended sampling times for particular VOCs. For some more volatile VOCs, a standard tube may not have the capacity to sample for a full 8 hours (note that an 8-hour TWA concentration may be derived from the results of two or more consecutive samples, as described in HSG173[19]).

Calibration of pump

43 Calibrate the pump with a representative sorbent tube assembly in line, using an appropriate external calibrated meter (paragraph 24). One end of the calibrated flow meter should be at atmospheric pressure to ensure proper operation.

Blanks

44 Field blanks should be prepared by using tubes identical to those used for sampling and subjecting them to the same handling procedure as the samples except for the actual period of sampling. Label these as blanks.

Preparation of sampling equipment

45 Break open both ends of the sample tube, ensuring that each opening is at least one half the inside diameter of the tube. Insert the tube into its protective holder and attach to the sampling pump with the connecting tubing such that the back-up (50 mg) section is nearest the pump and ensuring that no leaks can occur. If sampling is not to start immediately, seal the open end of the sample tube with a protective end-cap.

Collection of samples

46 Fix the sampler to the worker, on the lapel and as close to the mouth and nose as possible. Then, either place the sampling pump in a convenient pocket or attach it to the worker in a manner that causes the minimum inconvenience, eg to a belt around their waist. When ready to begin sampling, remove the protective end-cap from the

sampler and switch on the pump. Record the time at the start of the sampling period, and if the pump is equipped with an elapsed time indicator, ensure that this is set to zero.

47 Since it is possible for a sample tube to become clogged, monitor the performance of the sample periodically, a minimum of every two hours. Measure the flow rate with the calibrated flowmeter and record the measured value. Terminate sampling and consider the sample to be invalid if the flow rate is not maintained to within ±5% of the nominal value throughout the sampling period.

48 Regular observation of the flow fault indicator is an acceptable means of ensuring that the flow rate of flow-stabilised pumps is maintained satisfactorily, provided that the flow fault indicator indicates malfunction when the flow rate is outside ±5% of the nominal value.

49 At the end of the sampling period, measure the flow rate with an accuracy of ±5% using the calibrated flowmeter, switch off the sampling pump, and record the flow time and the time. Also observe the reading on the elapsed time indicator, where fitted. Consider the sample to be invalid if the reading on the elapsed time indicator and the timed interval between switching on and switching off the sampling pump do not agree to within ±5%, since this may suggest that the sampling pump has not been operating throughout the sampling period. Reseal the sampler with its protective cover and disconnect it from the sampling pump.

50 Carefully record the sample identity and all relevant sampling data. Calculate the mean flow rate by averaging the flow rate measurements throughout the sampling period and calculate the volume of air sampled, in litres, by multiplying the flow rate in l/min by the sampling time in minutes.

51 With each batch of ten samples, submit for analysis at least two unused samplers from the same lot of tubes used for sample collection. Subject these blank samplers to the same handling procedure as the samples, but draw no air through them.

52 Record air temperature and barometric pressure periodically during sampling if it is desired either to express concentrations reduced to specific conditions (paragraph 72) or to express concentrations in volume fraction (paragraph 73).

Transportation and storage

53 There are no special requirements for transportation. Samples of very volatile materials, such as vinyl chloride, should be stored in dry ice; for less volatile materials, refrigeration is sufficient. If samples are not to be analysed within 8 hours, they are to be placed in a clean, uncoated, sealed metal or glass container.

ANALYSIS

54 Wear disposable gloves during analysis to reduce the possibility of contamination and to protect the hands from harmful solvents/reagents.

Cleaning of glassware

55 Before use, clean all glassware to remove any residual grease or chemicals. Soak overnight in laboratory detergent solution and then rinse thoroughly with water.

Preparation of sample and blank solutions

Desorption

56 Pipette 1.0 ml of desorption solvent (paragraph 35) into a septum vial of suitable capacity and cap the vial immediately. Score the sorbent tube containing the sample in the front (largest) section and break open the tube. Remove the glass wool and discard it. Open the vial and transfer the front section of sorbent into the desorption solvent and re-cap it. Agitate the vial occasionally over a period of 30 minutes to ensure maximal desorption. Repeat the same procedure for the second, back-up section, using a different vial. Desorb the sample blanks in the same way as the samples. In each case, carry out the desorption in a clean atmosphere in a fume hood.

57 When using sorbent tubes containing more than 150 mg (100 + 50 mg) sorbent, use a larger vial and a larger volume of desorption solvent pro rata. Other volumes of desorption solvent may be used for special applications.

58 For the desorption of samples of very volatile materials, such as vinyl chloride, the vial and desorption solvent should be pre-chilled before the addition of the sorbent.

Preparation of calibration standards

59 Prepare at least six calibration standards to cover the range of applicability. In air concentration (mg/m^3), this range will vary with the relevant exposure limit - see Table 1. For an example VOC with a limit value of 100 mg/m^3, a 10 l sample collected and desorbed in 1 ml will result in a solution of 1 mg/ml. To cover a typical range of 0.1-2 times the limit value, solutions in the range 0.1-2 mg/ml will be needed.

60 Standard solutions 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 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.

61 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 ±3%.

62 An internal standard is optional. It must not interfere with the compounds of interest and it must not be removed from the elution solvent by the sorbent. In the context of this method, the purpose of the internal standard is to correct for small variations in the injection volume. 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 recommended. Desorption efficiency should be determined directly with the compounds of interest (paragraph 72).

63 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, m-ethyltoluene, o-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.

Chromatography

64 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 given in paragraph 30. Typical operating conditions for these columns might be temperature programming from 50-200°C at 5°C/min with a carrier gas flow of 0.7-0.8 ml/min helium.

System calibration

65 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%.

66 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, 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.

Samples

67 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. Where high VOC concentrations are found, dilute the sample solutions with solvent to bring the concentration back within the calibration range. Repeat the analysis and record the dilution factor.

68 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 4. 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.

69 If the back-up section contains more than 10% of the sample, discard that sample as unreliable.

CALCULATION OF RESULTS

Volume of air sample

70 Calculate the volume, *V*, in litres, of each air sample.

Concentration of VOC in air

Mass concentration of analyte

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

Then:

$$\text{concentration of VOC in air } (\text{mg/m}^3) = \frac{1000\,(m_{\text{front}} + m_{\text{back}} - m_{\text{blank}})}{D \times V}$$

where:
C = concentration of VOC in air (mg/m^3);
m_{front} = weight (µg) of VOC on sample tube front section;
m_{back} = weight (µg) of VOC on sample tube back section;
m_{blank} = weight (µg) of VOC on blank tube;
D = desorption efficiency, as read from the desorption efficiency curve, taking m_{front} as the weight recovered;
V = volume of air sampled (litres).

72 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 = the actual pressure of the air sampled, in kPa;
T = the actual temperature of the air sampled, in Kelvin.

Volume concentration of analyte

73 Alternatively, the concentration of VOC in the sampled air may be expressed in ppm.

$$\text{Concentration of VOC in air (ppm)} = C \times \frac{24.5}{M} \times \frac{T}{298} \times \frac{101}{P}$$

where:

24.5 = molar volume (litres) at 298 K and 101 kPa;
M = molecular mass of VOC.

METHOD PERFORMANCE

Determination of the breakthrough volume

74 The source references in Tables 2 and 3 give typical values for the breakthrough volumes, and hence suitable sampling flow rates and sampling times, of single VOC components. These breakthrough volumes may be concentration dependent. Where mixtures of non-polar analytes are sampled together, the mutual concentration effect on breakthrough volume is generally negligible. However, polar compounds, and especially high humidity, may reduce breakthrough volumes of non-polar analytes significantly. If the composition of a mixture of polar and non-polar analytes is known approximately, breakthrough volumes should be established with a similar mixture. More information on the determination of breakthrough volumes is given in Appendix 2.

Desorption efficiency

75 The source references in Tables 2 and 3 give typical values for the desorption efficiency of single VOC components. These desorption efficiency values may be concentration dependent. Where mixtures of non-polar analytes are desorbed with pure carbon disulphide, the mutual concentration effect on *D* is generally negligible. If the composition of a mixture of polar and non-polar analytes is known approximately, *D* values should be established with a similar mixture. More information on the determination of desorption efficiency is given in Appendix 3.

Detection limits

76 The qualitative and quantitative detection limits for VOCs, defined as three times and ten times the standard deviation of a blank determination, have not been determined systematically, as the blank is normally insignificant compared with the measured concentrations. Instead, method performance has normally been established over the range 0.1-2.0 x the US Permissible Exposure Limit (see paragraph 79).

Overall uncertainty

77 The overall uncertainty for a measuring procedure is defined in BS EN 482 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.[25]

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

where :
$\bar{x}$ 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.

78 An additional 5% is usually added to the overall uncertainty percentage calculated using the equation in paragraph 77, to allow for the variability of the pump flow rate. 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 0.1-0.5 LV and ±30% for samples in the range 0.5-2.0 LV (LV = limit value).[12]

79 The method has been examined as part of the NIOSH Standards Completion Programme.[17] This gives values of between approximately 5 and 10% for the combined pump and analytical precision (as a coefficient of variation) over the range 0.1-2.0 x the US Permissible Exposure Limit (PEL). In most cases, the PEL is equivalent to exposure limits in other countries.

80 The NIOSH Standards Completion Programme acceptance criterion is broadly equivalent to overall uncertainty in EN 482,[25] using the test methods in EN 1076.[26] Allowing 5% for the maximum bias expected, the overall uncertainty (EN 482) will always be within 30%. However, biases greater than 5% may be introduced through the use of incorrect desorption efficiencies (see paragraph 75).

Interferences

81 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.

82 High humidity may affect the recovery of some compounds from samplers, particularly for those using activated charcoal. The original method validation (eg references 17 and 18) should be consulted for specific advice.

Stability of calibration blends

83 Calibration blends 1-3 (paragraph 63) are stable for at least one year when stored in dark glass bottles with PTFE-lined screw-caps below 4°C.

Stability of calibration solutions

84 Storage times for calibration solutions vary according to application. Typically, carbon disulphide dilutions should be freshly prepared weekly, or more frequently if evidence is noted of decomposition or evaporation.

QUALITY CONTROL MEASURES

85 An appropriate level of quality control should be employed when using this method. Analytical quality requirements, guidance on the establishment of a quality assurance programme and details of internal quality control and external quality assessment schemes are fully described in MDHS 71.[27]

86 It is strongly recommended that all laboratories undertaking the determination of hazardous substances in workplace air should participate in an external quality assessment scheme such as HSE's Workplace Analysis Scheme for Proficiency (WASP). Details of WASP are given in MDHS 71.[27]

TEST REPORT

87 Appendix 4 gives recommendations for information to be included in the test report.

Table 1 Limit values and published HSE guidance by compound name

Compound name	*HSE Guidance Note EH40 limit values*[12]					*Other HSE guidance*[3, 6, 11]
	MEL or OES	*long-term*		*short-term*		
		ppm	*mg/m^3*	*ppm*	*mg/m^3*	
Acetic acid	OES	10	25	15	37	
Acetone	OES	750	1810	1500	3620	EH64/D2
Acetonitrile	OES	40	68	60	102	
Acrylonitrile	MEL	2	4.4			EH64/C2
Allyl alcohol	OES	2	4.8	4	9.7	
2-Aminoethanol	OES	3	7.6	6	15	
Aniline	MEL	1	4			EH64/C57, EH72/8
Benzene	MEL	5	16			EH64/C5, TR4
Benzyl chloride (α-Chlorotoluene)						EH64/E20*
Bornan-2-one (Camphor)	OES	2	13	3	19	
Bromochloromethane (Chlorobromomethane)	OES	200	1080	250	1340	**
Bromoform	OES	0.5	5.3			
Bromotrifluoromethane (Trifluorobromomethane)	OES	1000	6190	1200	7430	
Butadiene	MEL	10	22			EH64/C7
Butan-1-ol (n-Butyl alcohol)	OES			50	154	EH64/D9
Butan-2-ol (sec-Butyl alcohol)	OES	100	308	150	462	
2-Butoxyethanol	OES	25	123			EH64/D90, TR10
Butyl-2,3-epoxypropyl ether (Butyl glycidyl ether)	OES	25	135			
n-Butyl acetate	OES	10	53			
sec-Butyl acetate	OES	200	966	250	1210	
Carbon disulphide	MEL	10	32			EH64/C8, TR3
Carbon tetrachloride	OES	2	13			EH64/D11, EH65/10
1-Chloro-2,3-epoxypropane (Epichlorohydrin)	MEL	0.5	1.9	1.5	5.8	EH64/C38, EH65/6
Chlorobenzene	OES	50	234			EH64/D15
2-Chlorobuta-1,3-diene (β-Chloroprene)	OES	10	37			
Chlorodifluoromethane	OES	1000	3590			EH64/D16, EH65/7

Compound name	*HSE Guidance Note EH40 limit values*[12]					*Other HSE guidance*[3, 6, 11]
	MEL or OES	*long-term*		*short-term*		
		ppm	*mg/m^3*	*ppm*	*mg/m^3*	
Chloroethane (Ethyl chloride)	OES	1000	2700	1250	3380	
2-Chloroethanol (Ethylene chlorohydrin)	OES			1	3.4	EH64/D17
Chloroform	OES	2	9.9			EH64/D18, EH65/11
Chloromethane (Methyl chloride)	OES	50	105	100	210	
Cresols, all isomers	OES	5	22			
Cryofluorane (1,2-Dichlorotetrafluoroethane)	OES	1000	7110	1250	9980	
Cumene	OES	25	125	75	375	EH64/D21, EH65/8
Cyclohexane	OES	100	350	300	1050	EH64/D23
Cyclohexanol	OES	50	208			
Cyclohexanone	OES	25	102	100	408	
Cyclohexene	OES	300	1020			
Dibromodifluoromethane (Difluorodibromomethane)	OES	100	872	150	1310	
Dibromoethylene (Ethylene dibromide)	MEL	0.5	3.9			EH64/C10
1,2-Dichlorobenzene	OES			50	306	EH64/D25
1,4-Dichlorobenzene	OES	25	153	50	306	EH64/D26, EH65/9
Dichlorodifluoromethane	OES	1000	5030	1250	6280	
1,1-Dichloroethane	OES	200	823	400	1650	EH64/D27, EH65/4
1,2-Dichloroethane (Ethylene dichloride)	MEL	5	21			EH64/C36
1,2-Dichloroethylene	OES	200	806	250	1010	
Dichlorofluoromethane	OES	10	43			
Dichloromethane (Methylene chloride)	MEL	100	350	300	1060	EH64/C37, EH64/E19,* EH74/1
Diethyl ether (Ethyl ether)	OES	400	1230	500	1540	EH64/D74
Diethylamine	OES	10	30	25	76	EH64/E24*
2-Diethylaminoethanol	OES	10	49			
Diisopropyl ether (Isopropyl ether)	OES	250	1060	310	1310	
Dimethoxymethane (Methylal)	OES	1000	3160	1250	3950	
Dimethyl sulphate	MEL	0.05	0.26			EH64/C45, EH65/27
Dimethylacetamide	OES	10	36	20	72	EH64/D68, EH65/3
N,N,-Dimethylaniline	OES	5	25	10	50	
Dimethylanmine	OES	10	19			EH64/24
2,6-Dimethylheptan-4-one (Diisobutyl ketone)	OES	25	148			
Dioxane	OES	25	91	100	366	
Diphenyl	OES	0.2	1.3	0.6	3.8	
2,3-Epoxypropyl isopropyl ether (Isopropyl glycidyl ether)	OES	50	241	75	362	
Ethanol	OES	1000	1920			
2-Ethoxyethanol	MEL	10	37			EH64/C12, TR10
2-Ethoxyethyl acetate	MEL	10	55			EH64/C13, TR10
Ethyl acetate	OES	400	1460			EH64/E26*
Ethyl acrylate	OES	5	21	15	62	
Ethyl formate	OES	100	308	150	462	
Ethylbenzene	OES	100	441	125	552	
Ethylene glycol dinitrate	OES	0.2	1.3	0.2	1.3	
Furfuryl alcohol	OES	5	20	15	61	
Heptan-2-one (Methyl n-amyl ketone)	OES	50	237	100	475	EH64/D76
Heptan-3-one (Ethyl butyl ketone)	OES	50	237	100	475	EH64/D76
Heptane	***					
Hexachloroethane (vapour)	OES	5	49			
n-Hexane	OES	20	72			EH64/D34
2-Hexanone	OES	5	21			
4-Hydroxy-4-methylpentanone (Diacetone alcohol)	OES	50	241	75	362	
Iodomethane (Methyl iodide)	MEL	2	12			EH64/C49, EH65/25
Isopentyl acetate (Isoamyl acetate)	OES	100	541	125	67	

Compound name	HSE Guidance Note EH40 limit values[12]					Other HSE guidance[3, 6, 11]
	MEL or OES	long-term		short-term		
		ppm	mg/m^3	ppm	mg/m^3	
Isopentyl acetate (Isobutyl acetate)	OES	150	724	187	903	
Isopropyl acetate	OES			200	849	EH64/D40
Kerosene	***					
Methanol	OES	200	266	250	333	
2-Methoxyethanol	MEL	5	16			EH64/C21, TR10
2- Methoxyethyl acetate	MEL	5	25			EH64/C22, TR10
2-Methoxymethyl-methoxy propanol						EH64/E27*
1-Methoxypropyl acetate						EH64/E28*
Methyl acetate	OES	200	616	250	770	
Methyl acrylate	OES	10	36			EH64/D45
Methyl t-butyl ether	OES	25	92	75	275	EH64/D98
Methyl methacrylate	OES	50	208	100	416	EH64/D80, EH65/16
3-Methylbutan-1-ol (Isoamyl alcohol)	OES	100	366	125	458	
1-Methylbutyl acetate (sec-Amyl acetate)	OES			150	812	
Methylcyclohexane	***					
Methylcyclohexanol	OES	50	237	75	356	
Methylcyclohexanone	OES	50	233	75	350	
5-Methyl-3-heptanone	OES	25	133			
4-Methylpent-3-en-2-one (Mesityl oxide)	OES	15	61	25	102	
4-Methylpentan-2-ol (Methyl isobutyl carbinol)	OES	25	106	40	170	
4-Methylpentan-2-one (Methyl isobutyl ketone)	OES	50	208	100	416	EH64/D81
2-Methylpropan-2-ol (t-Butyl alcohol)	OES	100	308	150	462	
2-Methylpropan-1-ol (Isobutyl alcohol)	OES	50	154	75	231	
1-Methyl-2-pyrrolidone (N-Methyl-2-pyrrolidone)	OES	25	103	75	309	EH64/D102, EH72/10
Methylstyrenes, all isomers except α-methylstyrene	OES	100	491	150	736	
Naphthalene						EH64/D104, CHAN 12
Nicotine	OES		0.5		1.5	
Nitrobenzene	OES	1	5.1	2	10	
Nitroethane	OES	100	312			
Nitroglycerine	OES	0.2	1.9	0.2	1.9	
2-Nitropropane	MEL	5	19			EH64/C40
Nitrotoluene(s)	OES	5	29	10	57	
Octane	***					
Pentan-2-one (2-Pentanone)	OES	200	716	250	895	
Pentane						
Pentyl acetates (Amyl acetates)	OES	100	541	150	812	EH64/E29*
Petroleum ether	***					
Phenol	OES	5	20	10	39	
Phenyl 2-3-epoxypropyl ether (Phenyl glycidyl ether)	OES	1	6.2			
2-Phenylpropene (α-Methylstyrene)	OES			100	491	EH64/D52
Propan-1-ol (n-Propyl alcohol)	OES	200	500	250	625	
Propan-2-ol (Isopropyl alcohol)	OES	400	999	500	1250	
n-Propyl acetate	OES	200	849	250	1060	
Propylene oxide	MEL	5	12			EH64/C52, EH65/21
Pyridine	OES	5	16	10	33	
Rubber solvent	***					
Styrene	MEL	100	430	250	1080	EH64/C26, TR1
p-tert-Butyltoluene	***					
1,1,2,2-Tetrabromoethane	OES	0.5	7.2			
1,1,2,2-Tetrachloro-1,2- difluoroethane	OES	100	847	100	847	
1,1,1,2-Tetrachloro-2,2- difluoroethane	OES	100	847	100	847	
Tetrachloroethylene	OES	50	345	100	689	EH64/D93

Compound name	*HSE Guidance Note EH40 limit values*[12]					*Other HSE guidance*[3, 6, 11]
	MEL or OES	*long-term*		*short-term*		
		ppm	*mg/m^3*	*ppm*	*mg/m^3*	
Tetrahydrofuran	OES	100	300	200	599	EH64/D89
Toluene	OES	50	91	150	574	EH64/D63
o-Toluidine	MEL	0	0.89			EH64/C54, EH65/20
1,2,4-Trichlorobenzene						EH 64/E30*
1,1,2-Trichloro-2,2-trifluoroethane	OES	1000	770	1250	9740	
1,1,1-Trichloroethane	OES	200	1110	400	2220	EH64/D94, TR9
Trichloroethylene	MEL	100	430	150	820	TR6
Trichlorofluoromethane (Fluorotrichloromethane)	OES	1000	5710	1250	7140	
1,2,3-Trichloropropane	OES	50	306	75	460	
3,5,5-Trimethylcyclohex-2-enone (Isophorone)	OES			5	29	EH64/D65
Turpentine	OES	100	566	150	850	
Vinyl acetate	OES	10	36	20	72	
Vinyl chloride	MEL	7				EH63, EH64/C29
Vinylidine chloride	MEL	10	40			EH64/C30
Xylene	OES	100	441	150	662	EH64/D67
2,4-Xylidine	OES	2	10	10	50	EH64/C28

* OEL under review - see *COSHH 1999: Proposals for MELs, OESs and biological monitoring guidance values* HSE Consultative Document 150, included in EH64,[3] Part E.

** OEL under review.

*** See *Reciprocal calculation procedure for mixtures of hydrocarbon solvents*, Part 3 of EH40.[12]

Table 2 Published methods giving further information on sampling and analysis details for specific VOCs - HSE methods

Method name	*Test compounds*	*Sorbent**	*Desorption solvent*	*MDHS method no*[13]
Acrylonitrile	Acrylonitrile	C	CS_2	1
Benzene	Benzene	C	CS_2	17
Carbon disulphide	Carbon disulphide	C	toluene	15
Chlorinated hydrocarbons	Dichloromethane [a] Chloroform Carbon tetrachloride 1,1-Dichloroethane 1,2-Dichloroethane 1,1-Dichloroethylene 1,2-Dichloroethylene [a] 1,1,1-Trichloroethane 1,1,2-Trichloroethane Trichloroethylene 1,1,2,2-Tetrachloroethane [b] Tetrachloroethylene Chlorobenzene o-Dichlorobenzene	C	CS_2	28
	1,2-Dichoropropane [a,b]	C	85:15 cyclohexane: acetone	28
Dioctyl phthalates	Di(2-ethylhexyl)phthalate 'Diisooctyl' phthalate	T [c]	cyclohexane	32
Ethylene dibromide	Ethylene dibromide	T	hexane	45 [d]
Ethylene oxide	Ethylene oxide	C [e]	CS_2	26
Glycol ether and glycol ether acetates	2-Butoxyethanol 2-Ethoxyethanol 2-Methoxyethanol 2-Butoxyethyl acetate 2-Ethoxyethyl acetate 2-Methoxyethyl acetate	C	95:5 CH_2Cl_2:methanol	21

Method name	*Test compounds*	*Sorbent**	*Desorption solvent*	*MDHS method no*[13]
Styrene	Styrene	C	CS_2	20
Toluene	Toluene	C	CS_2	36
Vinyl chloride	Vinyl chloride	C [f]	CS_2	24

* C = charcoal (100 + 50 mg tube), T = Tenax (100 + 50 mg tube)

[a] 400 + 200 mg tube
[b] petroleum-based charcoal
[c] 200 mg or 30 + 15 mg tube
[d] analysis by CG/electron capture
[e] Columbia JXC charcoal
[f] 800 + 200 mg tube

Table 3 Published methods giving further information on sampling and analysis details for specific VOCs - NIOSH methods

*Method name**	*Test compounds**	*Sorbent***	*Desorption solvent*	*NIOSH method no*[17]
Acetone cyanohydrin		QS	ethyl acetate	2506 [k]
Acetic acid		C	formic acid	1603
Acetonitrile		C [f]	85:15 methylene chloride:methanol	1606
Acrylonitrile		C	98:2 CS_2:acetone	1604
Alcohols I	t-Butyl alcohol	C	99:1 CS_2:2-propanol	1400
	Isopropyl alcohol			
	Ethanol	C		
Alcohols II	n-Butyl alcohol	C	99:1 CS_2:2-propanol	1401
	Isobutyl alcohol			
	sec-Butyl alcohol			
	n-Propyl alcohol			
Alcohols III	Allyl alcohol	C	95:5 CS_2:2-propanol	1402
	Isoamyl alcohol			
	Methyl isobutyl carbinol			
	Cyclohexanol			
	Diacetone alcohol			
Alcohols IV	2-Butoxyethanol	C	95:5 CH_2Cl_2:methanol	1403
	2-Ethoxyethanol			
	2-Methoxyethanol			
Allyl chloride		C	methanol	1000
Amines Aliphatic	Diethylamine	S	dil H_2SO_4 in 10% aq. methanol	2010
	Dimethylanmine			
Amines Aromatic	Aniline	S	95% ethanol	2002
	o-Toluidine			
	2,4-Xylidine			
	N,N,-Dimethyl-p-toluidine			
	N, N,-Dimethylaniline			
Aminoethanol compounds I	2-Aminoethanol	S [m]	80% methanol	2007
	2-Dibutylaminoethanol			
	2-Diethylaminoethanol			
Anisidine		XAD-2 [n]	methanol	2514 [a]
Butadiene		C [f]	methylene chloride	1024
Butyl glycidyl ether		C	CS_2	1616
Carbon disulphide		C [o]	toluene	1600 [p]
β-Chloroprene		C	CS_2	1002
Cresols and phenol	o-Cresol	XAD-7	methanol	2546
	m-Cresol			
	p-Cresol			
	Phenol			

*Method name**	*Test compounds**	*Sorbent***	*Desorption solvent*	*NIOSH method no*[17]
Dichlorodifluoromethane etc	Dichlorodifluoromethane 1,2-Dichlorotetrafluoroethane Chlorodifluoromethane	C [c]	methylene chloride	1018
Dichlorofluoromethane		C [d]	CS_2	2516
1,1-Dichloro-1-nitroethane		C	CS_2	1601
Difluorodibromomethane		C [e]	2-propanol	1012
Dimethylacetamide		S	methanol	2004
Dimethyl sulphate		P	diethyl ether	2524[l]
Dioxane		C	CS_2	1602
Diphenyl		T [q]	carbon tetrachloride	2530
Epichlorohydrin		C	CS_2	1010
Esters I	n-Amyl acetate n-Butyl acetate 2-Ethoxyethyl acetate Ethyl acrylate Methyl isoamyl acetate n-Propyl acetate Isobutyl acetate sec-Amyl acetate sec-Butyl acetate Isoamyl acetate	C	CS_2	1450
Ethyl acetate		C	CS_2	1457
Ethyl bromide		C	2-propanol	1011
Ethyl chloride		C [f]	CS_2	2519
Ethylene chlorohydrin		C [g]	95:5 CS_2:2-propanol	2513
Ethylene dibromide		C	99:1 benzene:methanol	1008
Ethyl ether		C	ethyl acetate	1610
Ethyl formate		C	CS_2	1452
Fluorotrichloromethane		C [f]	CS_2	1006
Furfuryl alcohol		Q	acetone	2505
Glycidol		C	tetrahydrofuran	1608
Hexachlorobutadiene		XAD-2	hexane	2543 [h]
Hexachloro-1,3-cyclopentadiene		T [i]	hexane	2518 [h]
Hydrocarbons BP 36-126°	Benzene, Toluene Pentane thro' Octane Cyclohexane Cyclohexene Methylcyclohexane	C	CS_2	1500
Hydrocarbons Aromatic	Benzene Cumene Naphthalene α-Methylstyrene Styrene Vinyltoluene p-tert-Butyltoluene Ethylbenzene Toluene Xylene	C	CS_2	1501
Hydrocarbons Halogenated	Chloroform Tetrachloroethylene o- & p-Dichlorobenzene Bromoform Methyl chloroform Chlorobromomethane 1,2-Dichloroethane 1,1,1-Trichloroethane 1,1,2-Trichloroethane 1,2-Dichloroethylene Tetrachloroethylene Carbon tetrachloride Ethylene dichloride	C	CS_2	1003

*Method name**	*Test compounds**	*Sorbent***	*Desorption solvent*	*NIOSH method no*[17]
	Chlorobenzene Hexachloroethane 1,2,3-Trichloropropane			
Isophorone		C [g]	CS_2	2508
Isopropyl acetate		C	CS_2	1454
Isopropyl ether		C	CS_2	1618
Isopropyl glycidyl ether		C	CS_2	1620
Ketones I	Acetone Cyclohexanone Diisobutyl ketone 2-Hexanone Methyl isobutyl ketone 2-Pentanone	C	CS_2	1300
Ketones II	Camphor Ethyl butyl ketone Mesityl oxide 5-Methyl-3-heptanone Methyl n-amyl ketone	C	99:1 CS_2:methanol	1301
Methanol		S [r]	5% 2-propanol in water	2000
Methyl acetate		C	CS_2	1458
Methyl acrylate		C	CS_2	1459
Methylal		C	hexane	1611
Methyl cellosolve acetate	2-Methoxyethyl acetate	C	CS_2	1451
Methyl chloride		C [c]	methylene chloride	1001
Methyl cyclohexanol		C	methylene chloride	1401
Methyl cyclohexanone		Q	acetone	2521
Methylene chloride	Dichloromethane	C [j]	CS_2	1005
Methyl methacrylate		XAD-2 [f]	CS_2	2537
Methyl t-butyl ether		C [f]	CS_2	1615
Methyl iodide		C	toluene	1014
Naphthas	Kerosine Petroleum ether Rubber solvent Stoddard solvent, etc	C	CS_2	1550
Nicotine		XAD-2	ethyl acetate	2544 [k]
Nicotine		XAD-4	ethyl acetate + 0.01% triethylamine	2551 [k]
Nitro-aromatic compounds	Nitrobenzene Nitrotoluene(s) 4-Chloronitrotoluene	S	methanol	2005
Nitroethane		XAD-2 [s]	ethyl acetate	2526
2-Nitropropane		106	ethyl acetate	2528
Nitroglycerin and Ethylene glycol dinitrate		T	ethanol	2507
N-Methyl-2-pyrrolidone		C	95:5 methylene chloride: methanol	1302
1-Octane thiol		T	acetone	2510 [k]
Pentachloroethane		R	hexane	2517 [h]
Phenyl ether		C	CS_2	1617
Phenyl ether/diphenyl mixture		S	benzene	2013
Phenyl glycidyl ether		C	CS_2	1619
Propylene oxide		C	CS_2	1612
Propylene dichloride	1,2-Dichloropropane	C [g]	85:15 cyclohexane: acetone	1013 [l]
Pyridine		C	methylene chloride	1613
Terpenes	Limonene α-Pinene β-Pinene 3-Carene	C	CS_2	1552
1,1,2,2-Tetrabromoethane		S	Tetrahydrofuran	2003

*Method name**	*Test compounds**	*Sorbent***	*Desorption solvent*	*NIOSH method no*[17]
1,1,1,2-Tetrachloro 2,2-difluoroethane etc	1,1,1,2-Tetrachloro-2,2 1,1,2,2-Tetrachloro-1,2-difluoroethane	C	CS_2	1016
1,1,2,2-Tetrachloroethane		C [g]	CS_2	1019
Tetrahydrofuran		C	CS_2	1609
Trichloroethylene		C	CS_2	1022
1,1,2-Trichloro-1,2,2-trifluoroethane		C	CS_2	1020
Trifluorobromomethane		C [c]	methylene chloride	1017
Turpentine		C	CS_2	1551
Vinyl acetate		CMS	95:5 methylene chloride:methanol	1453
Vinyl bromide		C [f]	ethanol	1009
Vinyl chloride		C [e]	CS_2	1007
Vinylidine chloride	1,1-Dichloroethene	C	CS_2	1015

* Some names in the NIOSH list are different from those in EH40. See Table 1 for synonyms.

** C = charcoal (100 + 50 mg tube);
CMS = carbon molecular sieve (160 + 80 mg tube);
P = Porapak P (100 + 50 mg tube);
Q = Porapak Q (150 + 75 mg tube);
QS = Porapak QS (100 + 50 mg tube);
R = Porapak R (70 + 35 mg tube);
S = Silica gel (150 + 75 mg tube);
T = Tenax (100 + 50 mg tube);
106 = Chromosorb 106 (100 + 50 mg tube);
XAD-2 (100 + 50 mg tube);
XAD-4 (80 + 40 mg tube);
XAD-7 (100 + 50 mg tube).

[a] analysis by high pressure liquid chromatography/ultra-violet (HPLC/UV)
[b] analysis by gas chromatography/thermal conductivity (detection) (GC/TCD)
[c] two tubes 400/200 + 100/50 mg
[d] two tubes 400/200 + 400/200 mg
[e] two tubes, 150 + 150 mg
[f] 400 + 200 mg tube
[g] petroleum-based carbon
[h] analysis by GC/electron capture (detection) (ECD)
[i] two tubes 75 + 25 mg
[j] two tubes 100/50 + 100/50 mg
[k] analysis by GC/nitrogen-phosphorus detection (NPD)
[l] analysis by GC/conductivity (Hall)
[m] 300 + 150 mg tube
[n] 150 + 75 mg tube
[o] uses a sodium sulphate drying tube in front
[p] analysis by GC/flame photometric (detection) (FPD)
[q] 20 + 10 mg tube
[r] 100 + 50 mg tube
[s] 600 + 400 mg tube

Table 4 Retention indices of selected VOCs on BP-1 and BP-10 phases

	BP-1		*BP-10*
propane	300	propane	300
dichlorodifluoromethane (Freon 12)	311	dichlorodifluoromethane (Freon 12)	318
methyl chloride	348	1,2-dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	353
1,2-dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	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 (Freon 11)	482	trichlorofluoromethane (Freon 11)	503
enflurane	486	2,2-dimethylbutane	528
acetone	487	1,1,2-trichloro-1,2,2-trifluoroethane	528
2-methylbutane	488	dichlorofluoromethane (Freon 21)	532
iso-propanol	488	dimethylethanolamine	553
dichlorofluoromethane (Freon 21)	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 (Freon 113)	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

	BP-1		*BP-10*
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
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
furfuralmethoxyethyl acetate	807	hexanal	891
tetrachloroethene	807	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
ethoxyethyl 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	996	p-dichlorobenzene	1099
benzyl chloride	997	n-undecane	1100
n-decane	1000	1-methyl-2-isopropylbenzene	1104

	BP-1		*BP-10*
p-dichlorobenzene	1004	benzaldehyde	1105
p-dichlorobenzene	1004	1,3-diethylbenzene	1111
N-methyl-2-pyrrolidone	1009	indane	1117
1,2,3-trimethylbenzene	1019	propenylbenzene	1117
o-dichlorobenzene	1027	1,4-diethylbenzene	1118
o-cresol	1027	n-butylbenzene	1120
indane	1033	benzyl chloride	1128
1-methyl-2-iso-propylbenzene	1034	ethanediol diacetate	1130
indene	1039	o-dichlorobenzene	1135
propenylbenzene	1041	1,3-dimethyl-4-ethylbenzene	1146
p-cresol	1047	indene	1147
m-cresol	1047	benzyl chloride	1162
1,4-diethylbenzene	1051	butoxyethyl acetate	1185
n-butylbenzene	1052	n-dodecane	1200
butoxyethyl acetate	1061	phenol	1222
1,3-dimethyl-4-ethylbenzene	1075	1,1,2,3,4,4-hexachloro-1,3-butadiene	1270
vinyl pyrrolidone	1077	o-cresol	1274
nonanal	1085	2,6-xylenol	1296
2,6-xylenol	1093	tridecane	1300
n-undecane	1100	ethylhexyl methacrylate	1308
isophorone	1113	isophorone	1308
2,4-xylenol	1127	p-cresol	1311
2,5-xylenol	1127	m-cresol	1311
decanal	1129	vinyl pyrrolidone	1322
3,5-xylenol	1144	naphthalene	1328
2,3-xylenol	1158	2,4-xylenol	1360
3,4-xylenol	1171	2,5-xylenol	1360
2-(isopropyl)phenol	1175	2,3-xylenol	1400
naphthalene	1196	3,5-xylenol	1400
n-dodecane	1200	n-tetradecane	1400
ethylhexyl acrylate	1215	tetrahydrofurfuryl methacrylate	1400
1,1,2,3,4,4-hexachloro-1,3-butadiene	1223	3,4-xylenol	1434
n-tridecane	1300	2-methylnaphthalene	1447
2-methylnaphthalene	1310	1-methylnaphthalene	1470
1-methylnaphthalene	1328	n-pentadecane	1500
2,6-bis(isopropyl)phenol	1346	2,6-bis(isopropyl)phenol	1524
biphenyl	1388	biphenyl	1538
n-tetradecane	1400	n-hexadecane	1600
n-pentadecane	1500	n-hexadecane	1600

Notes

1 Retention index data for selected VOCs in Table 4 were compiled from HSL in-house sources. Most compounds listed in Tables 2 and 3 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 64. 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 OV 1701, equivalent to BP-10, are listed in MDHS 60.[28]

APPENDIX 1

Description of sorbent types

Sorbent	*Type*
Carbon	Coconut shell
Carbon	Petroleum-based
Anasorb 727*	Beaded microporous polymer with hydrophobic surface
Chromosorb 106*	Beaded microporous polymer with hydrophobic surface
Anasorb 747	Beaded active carbon derived from petroleum precursors
Silica gel	
Tenax TA	Poly (diphenyloxide)
Porapak R	

* believed to be equivalent

Anasorb™ is a trademark of SKC Inc, USA.
Chromosorb™ is a trademark of Manville Corp, USA.
Tenax™ is a trademark of Enka Research Institute, NV, NL.
Porapak™ is a trademark of Waters Associates Inc, USA.

APPENDIX 2

Determination of the breakthrough volume

The breakthrough volume for a sorbent tube/analyte combination is the volume of a vapour-in-air sample that can be passed through the front section of a sorbent tube before the eluting concentration of the analyte (VOC) vapour reaches 5% of the applied test concentration.

Prepare dynamic standard atmospheres of VOC vapour in air as in MDHS 3[29] or 4.[30] The temperature of the delivered concentration should be typical of the intended use of the sampler.

Assemble a sampling train consisting of the dynamic standard atmosphere generator delivering a concentration of twice the relevant exposure limit for the substance analysed, a sorbent tube (as in paragraph 16, but omitting the back-up section), a flow meter (range 20-200 ml/min) and a flame ionisation or similar detector.

Pass the gas through the sample train at a known constant rate between 20 ml/min and 200 ml/min. Use a value in this range which is suitable for the sampling rate intended (see paragraph 42). Note the time when the flow was initiated. When the VOC vapour begins to emerge, the detector will show a response. Continue the measurement until a plateau corresponding to the input concentration is reached or until the response is determined to be caused principally or totally by the VOC used. Determine the time at which 5% of the plateau value has been reached.

Usually, the dead volume of the sampling train is small in comparison with the breakthrough volume. If this is not the case, determine the dead volume by repeating the determination with an empty tube in the sampling train and correct the result accordingly.

Determine the effect of moisture on the breakthrough volume by humidifying the gas stream to approximately 80% relative humidity and repeating the test described above. Humidify the gas stream by diluting, in a ratio of 1:4 by volume, a primary gas stream at five times the concentration generated above with a stream of moist clean air at 100% relative humidity. Do not pass the VOC gas stream through water to humidify it.

The relative humidity specified (80%) is a practical value; it does not imply that the method is invalid at higher relative humidities, provided due attention is given to the restriction on sampling volumes at high humidity (paragraph 73).

Calculate the breakthrough volume by multiplying the flow rate in l/min by the time, in minutes, between zero and the moment when 5% of the plateau value has been reached.

APPENDIX 3

Determination of desorption efficiency

The desorption efficiencies (*D*) 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 *D* 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 *D* is a hidden variable, it is recommended that *D* 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 after addition. With some compounds the phase equilibrium method may give a higher value for *D* than direct spiking methods.[17-20]

D equals the weight (in µg) recovered divided by the weight (in µg) applied. Plot the *D* values against the weight recovered for each sampler load level. If the *D* at the load level is less than 0.75 (75%) a sample result corresponding to that level should be discarded (but see paragraph 51).

Where mixtures of non-polar analytes are desorbed with pure carbon disulphide, the mutual concentration effect on *D* is generally negligible. If the composition of a mixture of polar and non-polar analytes is known approximately, *D* values should be established with a similar mixture. It may not be possible to achieve greater than 75% *D* for all components of such a mixture with a single desorption solvent. Provided that it can be established that the *D* 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.

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.

APPENDIX 4

Recomendations for the test report

It is recommended that the test report should include the following information:

- complete identification of the sample, including the date and place of sampling;
- reference to this MDHS and a description of any deviation from the procedures described;
- the type and size of sample tube used;
- the type of sampling pump and flowmeter used, the primary standard against which it was calibrated, and the range of flow-rates for which the flowmeter was calibrated;
- the duration of the sampling time in minutes and/or the time at the start and at the end of the sampling period;
- the volume of air sampled, in litres;
- the name of the person who collected the sample;
- the time-weighted average concentration found in the air sample, in milligrams per cubic metre;
- the overall uncertainty of the method;
- the name of the analyst;
- the date of the analysis; and
- 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 (tel: 0114 2892000, fax: 0114 2892500, e-mail hslinfo@hsl.gov.uk).

The Health and Safety Executive wishes, wherever 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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