Volatile organic compounds in air

Laboratory method using sorbent tubes, solvent desorption or thermal desorption and gas chromatography

MDHS104

Methods for the Determination of Hazardous Substances

Health and Safety Laboratory

Scope

1   Three methods are described for the determination of time-weighted average concentrations of volatile organic compounds (VOCs) using air sampling onto sorbent tubes followed by gas chromatographic analysis. Method 1 uses pumped sampling with sample introduction by thermal desorption, Method 2 uses diffusive sampling also with sample introduction by thermal desorption and Method 3 uses pumped sampling and solvent desorption. All three methods are suitable for personal and static sampling.

2   These methods are applicable to a wide range of VOCs. For Methods 1 and 2, two sorbents are recommended for general use for hydrocarbons, halogenated hydrocarbons, esters, glycol ethers, ketones and alcohols. For Method 3 the most common sorbent used is activated coconut shell charcoal although others are available for specific applications.

Summary

3   A general guide to which of the three sorbent tube monitoring methods is appropriate for volatile organic compounds dependent upon required sampling time and estimated analyte concentration is given in Table 1.

4   The upper limit of the useful range of the three methods is determined by the sorptive capacity of the sorbent used and by the linear dynamic range of the gas chromatograph column and detector. The lower limit of the useful range depends on the noise level of the detector and on blank levels on the sorbent tubes or desorption solvent.

5   Method 1 (pumped sampling; thermal desorption) is suitable for sampling times of the order of a few minutes (0.1–100 mg.m^{-3}) up to 2 hours (low flow rate, approximate range 0.1–10 mg.m^{-3}. A measured volume of air is drawn through a sorbent tube containing appropriate sorbent, specifically selected for the compound or mixture to be sampled. The collected vapour is then thermally desorbed in an inert carrier gas into a gas chromatograph fitted with a suitable capillary column and detector.

6   Method 2 (diffusive sampling; thermal desorption) is suitable for samples of greater than 15 minutes up to 8 hours over a concentration range of approximately 1–1000 mg.m^{-3}. The sorbent tube, fitted with a diffusion cap, is exposed for a measured period of time, and then thermally desorbed in the same manner as Method 1.

7   Method 3 (pumped sampling; solvent desorption) is suitable for samples of a few minutes up to 8 hours over a concentration range of approximately 1–1000 mg.m^{-3}. A measured volume of air is drawn through a sorbent tube, which is then desorbed with a solvent, typically carbon disulphide for simple hydrocarbons.

8   In all three methods, the desorbed samples are quantified by gas
chromatography (GC) using either a flame ionisation (FID), mass selective (MS), or
other suitable detector.

9   The use of alternative methods not included in the MDHS series is acceptable
provided they can demonstrate the accuracy and reliability appropriate to the
application.

Recommended sampling

10   Method 1 (pumped sampling; thermal desorption): recommended sampling
rate: 50–100 ml.min^{-1}; typical sampled volume: 1 to 10 litres; maximum sampled
volume: see Tables 2a, 2b and 3 for details corresponding to Tenax TA, Carbopack
X and Chromosorb 106 sorbents respectively.

11   Method 2 (diffusive sampling; thermal desorption); minimum sampling time:
15 – 30 minutes (up to 8 hours); see Table 4 for details of diffusive uptake rates for
a range of analyte/sorbent combinations.

12   Method 3 (pumped sampling; solvent desorption); recommended sampling
rate: 50 – 200 ml.min-1; typical sample volume: 10 litres.

Prerequisites

13   Users of Methods 1 and 3 where pumped sampling is required will need to be
familiar with the content of MDHS14.[1]

Safety

14   Users of this method should be familiar with standard laboratory practice and
be able to carry out a suitable risk assessment. It is the user's responsibility to
establish appropriate health and safety practices and to ensure compliance with
regulatory requirements.

Equipment

Sorbent tubes

Methods 1 and 2

15   Pre-packed stainless steel sorbent tubes. Typically, the tubes should be
packed with 200 mg to 300 mg of a suitable sorbent (or sorbents) of particle size
0.18 mm to 0.5 mm (35 to 80 mesh). The sorbent is usually retained between two
steel gauzes. Each tube should have metal storage end caps fitted with PTFE
seals. The inlet end of the tube is usually marked by a scored ring about 10 mm
from the end. Ideally the tube should have a unique engraved/etched identification
number or bar code. Avoid the use of adhesive labels on the body of the tube that
can interfere with the tube transfer mechanism in the thermal desorption
equipment.

16   Diffusion end caps (Method 2 only). Standard end caps contain a metal gauze
only; special caps with an additional silicone membrane may be used to reduce
water uptake when using hydrophilic sorbents.

17   Select a sorbent tube appropriate for the compound or mixture and the required sampling duration. Guidance on selection of suitable sorbent tubes is given in Tables 2a, 2b, 3 and in EN ISO 16017-1[2] for active sampling and in table 4 and EN ISO 16017-2[3] for passive sampling. For active sampling, care should be taken to avoid breakthrough of the analyte and the recommended safe sampling volume (SSV) should be implemented. See Appendix 1 for further information on breakthrough volume and SSVs.

18   The industry standard stainless steel sorbent tube dimensions are typically either 3.5" (89 mm) long × ¼" (6.4 mm) OD × 5 mm ID or 7" (178 mm) long × 6 mm OD × 5 mm ID (not used passively, glass tubes with similar dimensions are also available). The air gap dimensions (distance between stainless steel screen retaining the sorbent bed and the inlet end of the tube) which is fundamental for accurate diffusive sampling should be in the range 14.0 mm to 14.6 mm. The diffusive uptake rates given in Table 4 are based on the 3.5" stainless steel tube. Additional information on the tube construction, dimensions, range of sorbent types and applicability are given in EN ISO 16017-1[2] or EN ISO 16017-2.[3]

19   The sorbent tubes should be conditioned according to the manufacturer's instructions before use, either on the instrument conditioning cycle or alternatively under a flow of dry inert gas such as nitrogen at typically 100 ml min-1 for 10 minutes with gas flow in the opposite direction to that used for sampling. The tube should be heated to a temperature usually at least 25 °C below the manufacturer's recommended maximum temperature for the sorbent but above the analysis desorption temperature and recapped immediately after cooling. Guidance on typical conditioning parameters for common sorbents is given in EN ISO 16017-1[2] or EN ISO 16017-2.[3]

20   For new tubes, after conditioning, a representative sample, (typically 10%) should be analysed to ensure that the thermal desorption blanks are acceptable. The sorbent tube blank level should be very low (eg <2 ng) but with use of high sensitivity detection methods very low sample amounts can be analysed. Rather than stating absolute values, it may be considered acceptable if interfering artefact peak areas are less than 5% of the typical area of the analyte(s). If levels of artefacts exceed these levels, reconditioning should be considered.

21   The desorption efficiency of the analyte from the sorbent tube will be quantitative (>95%) provided that appropriate desorption parameters are adopted. Typical desorption temperatures are given in Tables 2a, 2b and 3 for a range of organic compounds on Tenax TA, Carbopack X and Chromosorb 106 sorbents respectively. Information on additional sorbents can be found elsewhere.[2,3] The efficiency of desorption can be checked by analysing a clean empty glass tube (to identify that the analyte has been fully desorbed from the trap) after the sorbent tube, followed by reanalysis of the first tube to confirm quantitative desorption has been achieved by the first analysis. This should be repeated for a range of loadings to cover the calibration range of the method. Alternative procedures to determine desorption efficiency are described elsewhere.[2,3]

Method 3

22   A wide variety of pre-packed sorbent tubes for solvent desorption is commercially available, with coconut shell charcoal amongst the most widely used. Guidance on selection of suitable sorbent tubes is given in Table 5. Typical tubes are made of glass 70 mm to 110 mm long with an OD of 6 mm to 8 mm. The tubes are generally supplied with both ends flame sealed and usually containing

two sorbent beds, separated and held in place by glass wool or foam plugs. In the case of coconut shell charcoal, the front (sample) bed usually contains 100 mg of sorbent and the back-up bed 50 mg. When sampling, glass tubes should be held in a protective holder when sampling in order to prevent breakage.

23   There may be some batch-to-batch variation in sorptive capacity of coconut shell charcoal. Tubes from a single batch should ideally be used in each application. Sorbents other than charcoal are available and may be used for certain applications.[4]

24   The desorption efficiency (D) of sorbents may vary for type, batch and mass loading. It is therefore necessary to determine D for each sorbent and analyte over the sample concentration range. See Appendix 2 or BS ISO 16200-1[4] for procedures describing determination of D.

25   The sorbent tube sampling efficiency will be 100%, provided that the sampling capacity of the sorbent has not been exceeded. If this capacity is exceeded, breakthrough of vapour from the front section to the back-up section will occur. The breakthrough volume varies with ambient air temperature, relative humidity, concentration of sampled vapour and of other contaminants, and with the sampling flow rate. An increase in any of these parameters causes a reduction in the breakthrough volume (See Appendix 1 for further information on breakthrough volume). The back-up section may be used as a check on breakthrough under practical conditions.

26   Published methods and validation data giving detailed information on breakthrough volumes, sampling flow rates, sampling times and analysis for specific analytes are available from the US regulatory authorities, ie OSHA[5] and NIOSH.[6]

Other equipment

27   Personal sampling pumps that meet the requirements of BS EN ISO 13137.[7]

28   A portable flow meter calibrated against a primary standard, with a measurement uncertainty typically less than ±2%.

29   Flexible plastic tubing for making a leak-proof connection from the sorbent tube to the pump; belts or harnesses to facilitate attachment of sampling apparatus to sample subjects.

Laboratory reagents and apparatus

30   During analysis use only reagents of a recognised analytical quality.

31   Volatile organic compounds: for preparation of calibration standards.

32   Methanol: diluent for the preparation of sorbent tube standards (Methods 1 and 2; alternative solvents can be used when appropriate).

33   Carbon disulphide: for solvent desorption of sorbent tubes (Method 3)

34   A calibrated 5 µl syringe capable of dispensing accurate volumes between 1 µl and 5 µl: for preparation of spiked sorbent tube standards (Methods 1 and 2).

35   A range of volumetric flasks with caps or suba-seal closures, Class A complying with the requirements of BS EN ISO 1042.[8]

36   Piston operated micropipettes complying with the requirements of BS EN 8655-6:[9] for dispensing organic liquids for gravimetric preparation of standard solutions.

37   A 2 ml gas tight syringe fitted with a hypodermic needle tip: for dispensing carbon disulphide.

38   A balance calibrated against a primary standard: for the preparation of calibration standards. The balance should be capable of weighing to ±0.1 mg over the range 0 to 100 g.

39   Injection unit for preparation of standards by liquid spiking (Methods 1 and 2): A conventional gas-chromatographic injection port may be used in situ, or mounted separately. The carrier gas line should be retained. The back of the injection port should be adapted to fit the sample tube. This can be done by means of a compression coupling with an O-ring seal. Purpose made liquid spiking units are also commercially available.

40   Gas chromatograph (GC) with thermal desorption inlet (Methods 1 and 2; see paragraph 40) and/or split/splitless liquid injector for injection of liquid samples (Method 3): The gas chromatograph should be fitted with a flame ionisation, mass selective or other suitable detector and a capillary column suitable for separating the analytes of interest and background components.

41   Thermal desorption apparatus (Methods 1 and 2): For two-stage thermal desorption of the sorbent tubes and transfer of the desorbed vapours by inert gas flow to the gas-chromatograph capillary column. A typical apparatus consists of an auto-sampler which holds the tubes and loads them sequentially into a heated zone that is purged with inert carrier gas. The desorption time, temperature and flow rate can be pre-set according to the manufacturer's instructions for the substances and concentration range of interest. The sample, once desorbed from the tube, is concentrated onto a cold trap consisting of an appropriate sorbent (usually the same sorbent type as the air sampling tubes), before rapid heating and transfer by heated transfer line to the gas chromatography column.

42   Typical operating conditions for the three methods, based on Tenax TA, Carbopack X and Chromosorb 106 sorbent for Methods 1 and 2, and charcoal for Method 3, are listed below. The use of other columns and conditions are acceptable provided they have the accuracy and reliability appropriate to the application.

Methods 1 and 2

Desorb temperature	200 to 320 °C (sorbent dependent)
Desorption time	3 to 10 min
Desorption Flow 1	20 to 50 ml.min^{-1}. (Total flow through tube)
Transfer line	200 °C
Cold trap low	+10 °C to -10°C or lower
Cold trap high	250 to 300 °C
Cold trap sorbent	Typically 30 to 40 mg Tenax or Carbon type sorbent
Desorption Flow 2	50 ml.min^{-1}
Carrier gas	Helium
Split ratios	Split ratios between the sample tube and secondary trap and between the secondary trap and the analytical column should be selected dependent on expected atmospheric concentration as specified by the instrument manufacturer
Capillary column	Typically a 50 m column × 0.25 mm capillary column containing a 0.5 to 1 µm thick 100% dimethyl polysiloxane (non-polar) phase is suitable for a wide range of VOCs
GC oven	Typical for non-polar column: 50 °C, ramp 5 °C min^{-1} up to 250 °C

Method 3

Carrier gas	Helium or hydrogen; 1 ml.min^{-1}.
Inlet	Split/splitless
Injection volume	1 µl
Capillary column	As Method 1 and 2
GC oven	As Method 1 and 2

Preparation and sampling

Method 1 (pumped sampling; thermal desorption)

43   Note and record the unique engraved sorbent tube identification mark.

44   Remove both metal end caps from the tube. Store the end caps in a clean plastic bag.

45   Connect the sorbent tube outlet (end opposite the scored ring) to the sampling pump using the flexible tubing and mount the tube vertically, either in the worker's breathing zone within 200 mm of the nose and mouth or in a static location.

46   Accurately set the flow rate to between 20 and 100 ml.min^{-1} using the calibrated portable flow meter so that the recommended sample volume is taken in the required time. Higher flow rates will result in lower limits of detection, however, care should be taken not to exceed the safe sampling volume for the analyte(s). Typical sample volumes are between 1 and 10 litres.

47   Record the time, temperature, flow rate (and the barometric pressure if required) when the pump was turned on.

48   At the end of the sampling period, record the flow rate, turn the pump off, and record the time, temperature (and the barometric pressure if required).

49   Securely recap the sorbent tube with the metal end caps and note its unique marking.

50   Transport back to the laboratory with the blanks in an inert airtight container.

51   If securely capped, sample tubes may be stored at room temperature prior to analysis.

Method 2 (diffusive sampling; thermal desorption)

52   Immediately before sampling remove the storage metal end cap from the 'inlet' end the sorbent tube (identified by the scored ring) and fit the diffusion cap. Leave the other end capped. Store the end cap in a clean plastic bag.

53   For personal sampling, clip the tube in the worker's breathing zone, for example on a lapel or pocket within 200 mm of the breathing zone. The orientation is not critical but to minimise ingress of rain in outdoor applications, mount the closed end uppermost.

54   Record the time and temperature (and barometric pressure if required) at the start and end of the sampling period.

55   At the end of the sampling period replace the diffusion cap with the storage end cap.

56   Transport back to the laboratory with the blanks in an inert airtight container.

57   If securely capped, sample tubes may be stored at room temperature prior to analysis.

Method 3

58   Remove the ends of the glass sorbent tube, using the tube manufacturer's tube breaker/capper to avoid injury to fingers, and place in a suitable tube holder to carry out the sampling.

59   Mount the tube vertically to avoid channelling, either in the worker's breathing zone within 200 mm of the nose and mouth or in a static location.

60   Connect the sorbent tube outlet (as marked on the tube) to the sampling pump using the flexible tubing. The back-up section must be nearest to the pump. Accurately set the flow rate between 20 ml.min^{-1} and 200 ml.min^{-1} using the calibrated portable flow meter. Higher flow rates will result in lower limits of detection, however, care should be taken not to exceed the safe sampling volume for the analyte(s).

61   Record the time, temperature, flow rate (and the barometric pressure if required) when the pump was turned on.

62   At the end of the sampling period, record the flow rate, turn the pump off, and record the time, temperature (and barometric pressure if required).

63   Securely recap the sorbent tube, label and transport back to the laboratory with the blanks in an inert airtight container.

64   If securely capped, sample tubes may be stored at room temperature prior to analysis.

Blanks

65   Blanks should be prepared using sorbent tubes identical to those used for sampling and subjected to the same handling procedures except for the period of sampling.

66   A minimum of two field blanks should be included with a batch of ten samples.

Calibration

Methods 1 and 2

67   Sorbent tube standards for calibration purposes should ideally be prepared by loading known amounts of the analyte(s) onto sorbent tubes from standard atmospheres as this procedure more accurately resembles the practical sampling situation.[2] However, a more practicable way of preparing standards is by a liquid spiking procedure, as described below (paragraph 68), provided that the spiking procedure is reliable and traceable to primary standards of mass or volume. Additionally, confirmation of the validity of the calibration curve by comparison with reference materials or standards produced using standard atmospheres is recommended. Participation in an analytical proficiency testing scheme will also support the validation of the laboratory analytical procedure.

68   Prepare at least two separate gravimetric standard solutions of the analyte(s) in methanol. For example: accurately weigh approximately 1 g of the analyte(s) into a 100 ml volumetric flask starting with the least volatile substance. Make up to volume with methanol, stopper and mix. This stock solution may be serial diluted as necessary. A second stock solution may be prepared in the same way for example by accurately weighing 10 mg of the analyte(s) into a 100 ml volumetric flask.

69   The standard solutions should be refrigerated whilst not in use and allowed to reach room temperature before tube loading.

70   Fresh standard solutions should be prepared weekly, or more frequently if evidence of deterioration is observed, eg condensation reactions between alcohols and ketones.

71   Prepare loaded sorbent tube calibration standards by injecting aliquots of the standard solutions onto clean sorbent tubes using the calibrated syringe as follows: Fit a clean sorbent tube into the injection unit in a flow of purge gas, typically nitrogen, at 100 ml.min^{-1}. Inject 1–5 µl aliquots of the standard solution through the septum and leave for 5 minutes if using methanol as the dilution solvent. Recap with the thermal desorption instrument end caps ready for analysis. If other dilution

solvents are used, the purge time should be determined experimentally. The concentration range of the loaded tubes is dependent on the application, but will typically be between 0.05 and 1000 µg.

72   For substances which are gases at room temperature, sorbent tube standards can be prepared by the following procedure: fill a 1 ml gastight syringe with 1 ml of pure gas (bleed the gas from a cylinder of pure gas through a short length of silicone rubber tubing with the end immersed in a beaker of water. Flush out the tubing with the gas, then withdraw the gas sample by piercing the tubing with the syringe after slowly pumping the syringe several times to ensure all the air has been removed. Close the syringe when filled. Inject the measured volume of gas through a septum seal into a calibrated volumetric flask (eg 1 litre) and mix. Calculate the concentration of gas using the gas laws, ie 1 mole of gas at STP (standard temperature and pressure: 273 K and 101.3 kPa) occupies 22.4 litres. Withdraw appropriate volumes of the diluted gas into a gas tight syringe and spike onto the sorbent tube using the tube injection unit. Alternative procedures for preparing sorbent tube standards from gaseous substances are described elsewhere.[2]

73   Analyse the calibration standards with the identical analytical method to be used for the samples and measure the peak areas of the target compound(s). Plot the peak areas against the corresponding analyte content of the standard, in µg, and construct the line of best fit. The slope of this line is the detector response factor (R_F) for the analyte.

Method 3

74   Prepare standard solutions of the analyte(s) in the desorbing solvent, typically carbon disulphide, containing a suitable internal standard (if available) of similar volatility to the analyte(s). The internal standard should not be removed from the elution solvent by the sorbent and should be used to correct for variations in injection volume not desorption efficiency. The concentration range of the loaded tubes is dependent on the application, but will typically be between 1 and 5000 µg.

75   Prepare at least six calibration standards to cover the analytical range. Typically for an expected concentration in the region of 100 mg.m^{-3}, a 10 l sample collected and desorbed in 1 ml will result in a solution of 1 mg.ml^{-1}. A calibration range in the region of 0.1–2 mg.ml^{-1} will typically be needed.

76   It is recommended that a minimum of two separate standard solutions are prepared gravimetrically by adding pure compounds to volumetric flasks partially filled with solvent. Volatile compounds may be injected through a silicone septum to avoid evaporative losses. Further standard solutions can be prepared by serial dilution of the first.

77   Fresh standard solutions should be prepared weekly or more frequently if evidence of deterioration or evaporation is observed.

78   Analyse the calibration standards with the identical analytical method to be used for the samples and measure the peak areas of the target compound(s). Plot the peak areas against the corresponding analyte content of the standard, in µg, and construct the line of best fit. The slope of this line is the detector response factor (R_F) for the analyte.

79   Check the calibration graph by analysing an independently prepared control sample. If the result does not agree with the calibration line within 10%, prepare fresh standards and carry out a new calibration.

80   Modern GC - FID equipment is usually sufficiently stable that a new calibration is not required with each set of samples. However, to verify system performance, a quality assurance (QA) standard or standard reference material must be analysed with each set of samples.

Sample analysis

Methods 1 and 2

81   Analyse the samples, QA samples and blanks in an identical manner to the calibration samples.

82   Measure the chromatographic peak area of the target compound(s) and convert this peak area to analyte mass, in µg, by dividing by the RF value obtained from the calibration standards.

83   Calculate the mean mass of the analyte, in µg, in the blanks.

Method 3

84   Desorb the samples, blanks and QA sample in the same way as soon as possible after sampling.

85   Score the sample tube just above the front (largest) section of sorbent and break open the tube, taking care not to lose any of the sorbent. Remove the glass wool and discard it. Transfer the front section of sorbent to a 2 ml septum vial and cap with a Teflon silicone septum.

86   Using a gas-tight syringe fitted with a needle tip, add 1 ml of solvent to the sorbent, injecting the solvent through the septum seal.

87   Agitate the vial occasionally over a period of 30 minutes to ensure maximum desorption.

88   Repeat the same procedure for the back-up section using a separate vial.

89   When using sorbent tubes containing more than 150 mg sorbent (100 + 50 mg), use a larger vial and solvent volume pro rata.

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

91   Analyse the samples, QA sample and blanks in an identical manner to the calibration samples.

92   Measure the chromatographic peak area of the target compound and convert this peak area to analyte mass, in µg, by dividing by the RF value obtained from the calibration standards.

93   Calculate the mean mass of the analyte, in µg, in the blanks.

Calculation of results

Method 1

94   Calculate the volume of air sampled for each sample, VS, in litres, by averaging the flow rate measurements throughout the sampling period and multiplying by the sampling time in minutes.

95   Calculate the airborne concentration of the analyte as a mass fraction, C, in mg.m^{-3}, using equation 1:

$$C = \frac{(M_S - M_B)}{V_S} \qquad\qquad \text{equation 1}$$

96   If it is desirable to express concentrations reduced to specified conditions (C_{corr}), eg 25 °C and 101 kPa, then:

$$C_{corr} = \frac{(C \times T \times 101)}{(298 \times P)} \qquad\qquad \text{equation 2}$$

97   Results may also be expressed as a volume fraction in air, C', in ppm, using equation 3:

$$C' = \frac{(C \times 24.5 \times T \times 101)}{(M_W \times 298 \times P)} \qquad\qquad \text{equation 3}$$

Where:

M_S = Mass of analyte in sample, in µg

M_B = Mean mass of analyte in blanks, in µg

V_S = Air volume of sample, in litres

24.5 = Molar volume of an ideal gas at 298 K, in litres

M_W = Molecular mass of analyte, in g.mol^{-1}

P   = Barometric pressure of the sampled air, in kPa

T   = Temperature of sampled air, in K

Method 2

98   Calculate the airborne concentration, as a mass fraction, of the analyte, C, in mg.m^{-3}, using equation 4:

$$C = \frac{(M_S - M_B)}{(U' \times t \times 1000)} \qquad\qquad \text{equation 4}$$

99   If it is desirable to express concentrations reduced to specified conditions (C_{corr}), eg 25 °C and 101 kPa, then using equation 5:

$$C_{corr} = \frac{(C \times 101 \times T)}{(298 \times P)}$$ equation 5

Where:

U' = Uptake rate in $cm^3 . min^{-1}$

t = Sampling period, in minutes

P = Barometric pressure of the sampled air, in kPa

T = Temperature of sampled air, in K

100 Calculate the airborne concentration, as a volume fraction, of the analyte, C', in ppm, using equation 6:

$$C' = \frac{(M_S - M_B)}{(U \times t \times 1000)}$$ equation 6

Where:

U = Uptake rate, in $ng.ppm^{-1}.min^{-1}$

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

$$U' (cm^3 . min^{-1}) = U (ng.ppm^{-1}.min^{-1}) \times \frac{(24.5 \times T \times 101)}{(M_W \times 298 \times P)}$$ equation 7

Method 3

101 Calculate the volume of air sampled for each sample, VS, in litres, by averaging the flow rate measurements throughout the sampling period and multiplying by the sampling time in minutes.

102 Calculate the airborne concentration of the analyte, C, in $mg.m^{-3}$, using equation 8:

$$C_{corr} = \frac{(M_{front} + M_{back} - M_{blank})}{(D \times V)}$$ equation 8

Where

C = concentration of VOC in air in in $mg.m^{-3}$

M_{front} = mass (µg) of VOC on sorbent tube front section

M_{back} = mass (µg) of VOC on sorbent tube back section

M_{blank} = mean mass (mg) of VOC on blank tubes

D = desorption efficiency, as read from the desorption efficiency curve taking M_{front} as the mass recovered (appendix 2)

V = volume of air sampled in litres

103 If it is required to express the results reduced to specific conditions (C_{corr}), eg 25 °C and 101 kPa, then using equation 9:

$$C_{corr} = \frac{(C \times T \times 101)}{(298 \times P)} \qquad \text{equation 9}$$

104 Results may also be expressed as a volume fraction in air, C', in ppm, using equation 10:

$$C' = \frac{(C \times 24.5 \times T \times 101)}{(M_W \times 298 \times P)} \qquad \text{equation 10}$$

Where:

24.5 = Molar volume of an ideal gas at 298 K, in litres

M_W = Molecular mass of analyte, in $g.mol^{-1}$

P = Barometric pressure of the sampled air, in kPa

T = Temperature of sampled air, in K

Detection limits

105 The estimated limit of detection (LOD) and limit of quantification (LOQ) may be calculated from the mean and standard deviation (SD) of the blanks using the following formulae:

$LOD = M_B + (3 \times SD)$

$LOQ = M_B + (10 \times SD)$

Where:

M_B = mean of 3 or more blanks

Interferences

106 Organic compounds that have the same or nearly the same retention time as the analyte of interest during the gas chromatographic analysis will interfere. Interferences can be minimised by good selection of gas chromatographic columns and conditions. In the case of Method 3, the solvent used for desorption should be checked beforehand to ensure it is of sufficient purity and does not contain potential interferences, eg carbon disulphide may often contain low concentrations of benzene.

107 High humidity will affect the recovery of some compounds from samplers, particularly for those using activated charcoal (Method 3). The method description should be consulted for specific advice.

Summary of data on overall uncertainty, precision, bias and storage

Method 1 – Pumped sampling

Data on overall uncertainty

108 Laboratory tests,[13] following in part EN 1076,[14] using tubes spiked from a standard atmosphere of hexane at 1.0 mg.m^{-3} and 50% R.H. at 20°C, indicated an uncertainty, expressed as an overall uncertainty from the mean of five determinations,[12] for Tenax TA, Tenax GR and Chromosorb 106 of 8.9%.

Data on precision and bias

109 The results of laboratory tests on tubes liquid spiked with a range of compounds on Tenax TA at a loading of approximately 10 µg are given in Table 6. The precision, expressed as a coefficient of variation, was between 0.4% and 2.8%, depending on the analyte. Expressed as repeatability[15], the range is equivalent to 1.1% to 5.6%.

110 Laboratory tests[16] were conducted on tubes liquid spiked with 80 ng or 200 ng of benzene, toluene and xylene, transported to field sites (in one survey, worldwide), exposed (closed) alongside sample tubes for 1 month and then returned to the laboratory for analysis. Recoveries for Chromosorb 106 and Carbograph TD-1 tubes were between 82.7 % and 105.9 %. The precision, expressed as a coefficient of variation, was between 3.2 % and 12.1 % depending on sorbent and analyte.

111 Additional information on precision and bias for other analytes and sorbents, including Chromosorb 106 and Carbograph TD-1, is given in EN ISO 16017-1.[2]

Storage

112 The results of laboratory tests on tubes liquid spiked with a range of compounds on Tenax TA at a loading of approximately 10 µg and stored at room temperature for 5 months are summarised in Table 6. Excluding hexane and methoxymethanol, the mean recovery, relative to unstored tubes, was 99.7% and the mean coefficient of variance was 2%. Similar results were obtained after storage for 11 months; excluding hexane and methoxymethanol, the mean recovery, relative to unstored tubes, was 99.4% and the mean coefficient of variance was 0.9%.

113 It is important to note that seals may become loose during refrigeration because of differential thermal contraction. To avoid loss of sample, or ingress of external contamination, caps or seals should be periodically checked.

114 Additional information on storage stability for other combinations of analytes and sorbents, including Chromosorb 106, is given in EN ISO 16017-1.[2]

Method 2 – Diffusive sampling

Data on overall uncertainty

115 Laboratory tests of the procedure, following EN 838,[11] yielded the diffusive uptake rates for individual organic compounds given in Table 4. It is important to note that different uptake rates may be given by other makes of diffusive tube, or if a silicone membrane is employed, or if a different sorbent is used.

116 Information on blank levels of benzene, toluene and xylene in Chromosorb 106 and Carbograph TD-1 are given in EN ISO 16017-2. For both sorbents, levels were in the low nanogram range.

Data on precision and bias

117 Laboratory tests[17] showed within batch repeatability, expressed as a coefficient of variation for six replicates, of between 0.5% and 2% for fourteen organic compounds, including aromatic hydrocarbons, chlorinated hydrocarbons, ketones, esters and glycol ethers, on Tenax TA and Chromosorb 106. Diffusive samples were taken from a standard atmosphere generated with an overall uncertainty of 3%. Between batch variability was between 2% and 12%. The between batch values equate to an overall uncertainty of between 6% and 24%.

118 Laboratory tests[18] on tubes liquid-spiked with benzene, toluene and xylene at 80 ng or 200 ng levels are summarized in EN ISO 16017-2 Table 3.[3] Tubes were transported to field sites (in one survey, world-wide), exposed (closed) alongside sample tubes for 1 month and then returned to the laboratory for analysis. Recoveries for Chromosorb 106 and Carbograph TD-1 tubes were between 82.7% and 105.9%. The precision, expressed as a coefficient of variation, was between 3.2% and 12.1% depending on sorbent and analyte.

119 Where Table 4 lists results at Level A or B, then the overall uncertainty as defined in EN 482[12] was better than 30%.

120 Note: For workplace measurements (Table 4), Level A is a full validation according to EN 838.[11] Level 1A, ie a laboratory evaluation of method performance (Level 1B allows for a homologue of a fully validated compound to comply with the standard). Level B in table 4 is a partial validation (where not all of the tests in EN 838 have been undertaken) allowed on a temporary basis by EN 482.[12]

Data on storage

121 See paragraphs 112–114.

Method 3 Solvent desorption

Precision and bias

122 The precision and bias of the method have been examined as part of the NIOSH Standards Completion Programme.[19] 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 to 2,0 times the US Permissible Exposure Limit (PEL). In most cases, the PEL is equivalent to Exposure Limits in other countries. Allowing 5% for the maximum bias expected, the overall uncertainty[12] will always be within 30%. However, biases greater than 5% may be introduced through the use of incorrect desorption efficiencies (see Appendix 2).

Storage and transport

123 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. Storage and transport in a refrigerator or freezer is not necessary for hydrocarbons and chloroalkanes on charcoal, but may improve storage stability for other analytes and/or sorbent types.

Quality control measures

124 An appropriate level of quality control should be employed when using this method. This should include recording the results of the analysis of any internal QA samples or reference materials.

125 It is strongly recommended that all laboratories undertaking the determination of hazardous substances in workplace air should participate in an external QA or proficiency testing scheme.

Appendix 1 Determination of breakthrough volume

1   The sampling efficiency for Methods 1–3 will be 100% (quantitative), provided the sampling capacity of the sorbents is not exceeded. If this capacity is exceeded, breakthrough of vapour from the tube assembly will occur. The breakthrough volume may be measured by sampling from a standard vapour atmosphere, whilst monitoring the effluent air with a flame ionization or equivalent detector.[2,4]

2   For porous polymers, the retention volume can be determined chromatographically at elevated temperatures and subsequent extrapolation to room temperature.[2,10] The breakthrough volume of porous polymers varies with ambient air temperature, reducing by a factor of about 2 for each 10 °C rise in temperature. It also varies with sampling flow rate, being reduced substantially at flow rates below 5 ml.min^{-1} or above 500 ml.min^{-1}.

3   The breakthrough volumes of carbon molecular sieves are less affected by temperature and flow rate, but are substantially reduced at high VOC concentrations or high relative humidity. To allow a suitable margin of safety, a safe sampling volume (SSV) is defined such that it is a volume of not more than 70% of the 5%-breakthrough volume or 50% of the retention volume (the breakthrough volume of a single injection of vapour).[2] Tables 2a and 3 give typical values for retention volumes and safe sampling volumes for Tenax and Chromosorb 106 sorbents respectively and also for these and other sorbents in EN ISO 16017-1.[2] These values have been determined by the chromatographic method.

4   Measurements by the direct method indicate that the chromatographic method is a reliable indication of the true breakthrough capacity except under conditions of high concentrations or very high humidity.[8] These measurements indicate that breakthrough volumes at high (80%) humidity are about a factor of two lower for porous polymers and a factor of ten lower for carbonaceous sorbents than the low humidity value. If high concentrations (>300 mg.m^{-3} (100 ppm)) are also anticipated, the breakthrough volumes for carbonaceous sorbents should be further reduced by a factor of two.

Appendix 2 Desorption efficiency

1   The desorption efficiency (D) of VOCs can vary with the type and batch of sorbent used. Thus it is necessary to determine D for each sorbent/analyte combination over the sample concentration range. If D is lower than 75% the tube shall not be used. Ideally, prepare loaded sorbent tubes for assessing desorption efficiency by passing an accurately known volume of a standard atmosphere at appropriate concentrations, temperature, humidity etc through the sorbent tube.[4] If the generation of standard atmospheres is not practicable then the procedure using liquid spiking can be utilised.

2   Alternatively, in the phase equilibrium method, accurately known volumes of standard solutions are added to the sorbent from samplers of the same batch by pipette and the difference in concentration measured before and after addition. If D is independent of concentration the pooled mean value over the concentration range can be used. Otherwise plot D against the mass of analyte recovered for each sampler loading level and D can be modelled using a smooth non-linear equation with D increasing with the ratio of analyte mass to sorbent mass. In such cases D can be estimated using this curve. Indicative values of D for single compounds are given in the published methods.[5,6] Actual values should always be determined at the time of analysis.

3   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 *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.

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

Table 1 General guidelines for the application of sorbent tube monitoring methods for volatile organic compounds dependent upon required sampling time (minutes) and analyte concentration (ppm)

Method	Sampling Period (min)	<0.1 ppm	0.1–1 ppm	1–100 ppm	>100 ppm
Method 1 (pumped sampling with thermal desorption)	<5	x	✓	✓	✓
	5–30	✓	✓	✓	(✓)
	30–60	✓	✓	(✓)	x
	>60	✓	(✓)	(✓)	x
Method 2 (diffusive sampling with thermal desorption)	<15*	x	x	x	x
	15–120	✓	✓	✓	✓
	120–480	✓	✓	✓	✓
	>480	✓	✓	✓	✓
Method 3 (pumped sampling with solvent desorption)	<15**	x	x	✓	✓
	15–120	x	x	✓	✓
	120–480	x	✓	✓	✓
	>480	x	x	x	x

Notes:

(✓) Sampling periods assume a typical flow rate of 50 ml/min and are guidance values only. It is essential to consider the safe sampling volume for each required analyte and not to exceed the capacity of the chosen sorbent.

* Sampling periods of less than 15 minutes are not recommended for diffusive samples because of the equilibrium time required.

Table 2a Extrapolated retention volumes and safe sampling volumes (SSV) for volatile organic compounds sampled on a 200 mg Tenax TA sorbent tube at 20 °C

Organic compound	Boiling point (°C)	Vapour pressure kPa (25 °C)	Retention volume (l)	SSV [a] (l)	SSV per gram (l.g⁻¹)	Desorption Temperature (°C)
Hydrocarbons						
Hexane	69	16	6.4	3.2	16	110
Heptane	98	4.7	34	17	85	130
Octane	125	1.4	160	80	390	140
Nonane	151	-	1400	700	3500	150
Decane	174	-	4200	2100	1.0×10^4	160
Undecane	196	-	2.5×10^4	1.2×10^4	6.0×10^4	170
Dodecane	216	-	1.3×10^5	6.3×10^4	3.0×10^5	180
Benzene	80	10.1	12.5	6.2	31	120
Toluene	111	2.9	76	38	90	140
Xylene	138 to 144	0.67 to 0.87	600	300	1500	140
Ethylbenzene	136	0.93	360	180	900	145
Propylbenzene	159	-	1700	850	4000	160
Isopropylbenzene	152	-	960	480	2400	160
Ethyltoluene	162	-	2000	1000	5000	160
Trimethylbenzene	165 to 176	-	3600	1800	8900	170
Styrene	145	0.88	600	300	1500	160
Methylstyrene	167	-	2400	1200	6000	170
Chlorinated hydrocarbons						
Carbon tetrachloride	76	12	12	6.2	31	120
1,2-Dichloroethane	84	8.4	11	5.4	27	120
Trichloroethylene	87	2.7	11.2	5.6	28	120
1,1,1-Trichloroethane	74	2.7	not recommended on Tenax			
1,1,2-Trichloroethylene	114	-	68	34	170	120
1,1,1,2-Tetrachloroethane	130	-	160	78	390	150
1,1,2,2-Terachloroethane	146	0.67	340	170	850	150
Trichloroethylene	87	2.7	11.2	5.6	28	120
Tetrachloroethylene	121	1.87	96	48	240	150
Chlorobenzene	131	1.2	52	26	130	140
Epichlorohydrin	118	-	26	13	65	130
Esters & glycolethers						
Ethyl acetate	71	9.7	7.2	3.6	18	120
Propyl acetate	102	3.3	36	18	92	140
Isopropyl acetate	90	6.3	12	6	31	120
Butyl acetate	126	1.0	170	85	420	150
Isobutyl acetate	115	1.9	265	130	650	130
t-Butylacetate	98	-	not recommended on Tenax			
Methyl acrylate	81	-	13	6.5	32	120

Organic compound	Boiling point (°C)	Vapour pressure kPa (25 °C)	Retention volume (l)	SSV [a] (l)	SSV per gram (l.g⁻¹)	Desorption Temperature (°C)
Ethyl acrylate	100	3.9	48	24	120	120
Methyl methacrylate	100	3.7	55	27	130	120
Methoxyethanol	125	0.8	6	3	15	120
Ethoxyethanol	136	0.51	10	5	25	130
Butoxyethanol	170	0.1	70	35	170	140
Methoxypropanol	118	-	27	13	65	115
Methoxyethyl acetate	145	0.27	16	8	40	120
Ethoxyethyl acetate	156	0.16	30	15	75	140
Butoxyethylacetate	192	0.04	300	150	750	160
Aldehydes & Ketones						
Methyl ethyl ketone	80	10.3	6.4	3.2	16	120
Methyl isobutyl ketone	118	0.8	52	26	130	140
Cyclohexanone	155	0.45	340	170	850	150
3,5,5-Trimethylcyclohex-2-enone	214	0.05	11000	5600	2800	90
Furfural	162	0.5	600	300	1500	200
Alcohols						
n-Butanol	118	0.67	10	5	25	120
Isobutanol	108	1.6	5.6	2.8	14	120
t-Butanol	83	1.17	not recommended on Tenax			
Octanol	180	-	2800	1400	7000	160
Phenol	182	0.03	480	240	1200	190
Others						
Bis(2-ethylhexyl) phthalate (and other similar phthalates **	385	6.7	VL	VL	VL	330
Diethyl sulphate	209	0.04	ND	ND	ND	150
Dimethyl sulphate	188	0.09	ND	ND	ND	150
Maleic anhydride	202	6.0×10^6	180	88	440	180
Pyridine	116	16	8	40	150	-
Aniline	184	0.09	440	220	1100	190
Nitrobenzene	211	0.02	28000	14000	70000	200

[a] reduce SSV by a factor of 2 if sampling at high humidity, see Appendix 1

** solvent desorption with cyclohexane recommended

ND = not determined but recommend 10 L air sample

VL = very large and fully retained by Tenax TA

Table 2b Extrapolated retention volume and safe sampling volume (SSV) for 1,3-butadiene sampled on a 200 mg Carbopack X sorbent tube at 20 °C

Organic compound	Boiling point (°C)	Vapour pressure kPa (25 °C)	Retention volume (l)	SSV [a] (l)	SSV per gram (l.g⁻¹)	Desorption Temperature (°C)
1,3-butadiene*	-4	245 (21 °C)	25	13	65	250

Table 3 Extrapolated retention volumes and safe sampling volumes (SSV) for volatile organic compounds sampled on a 300 mg Chromosorb 106 sorbent tube at 20 °C

Organic compound	Boiling point (°C)	Vapour pressure kPa (25°C)	Retention volume (l)	SSV [a] (l)	SSV per gram (l.g^{-1})	Desorption Temperature (°C)
Hydrocarbons						
Pentane	35	56	11.2	5.5	18	127
Hexane	69	16	60	30	100	140
Heptane	98	4.7	325	160	530	180
Octane	125	1.4	2076	1000	3300	200
Nonane	151	-	14000	7000	2.3×10^4	220
Decane	174	-	7.4×10^4	3.7×10^4	1.2×10^5	250
Benzene	80	10.1	53	26	87	160
Toluene	111	2.9	165	80	270	200
Xylene	138 to 144	0.67 to 0.87	1554	770	2600	250
Ethylbenzene	136	0.93	730	360	1200	250
Trimethylbenzene	165 to 176	-	5650	2800	9300	250
Chlorinated hydrocarbons						
Dichloromethane	40	47	4.2	2.1	7	120
Carbon tetrachloride	76	12	44	22	73	160
1,2-Dichloroethane	84	8.4	34	17	67	150
Epichlorohydrin	118	-	98	49	250	180
Trichloroethylene	-	27	80	40	140	170
1,1,1-Trichloroethane	74	13.3	54	27	89	160
Esters & glycolethers						
Methyl acetate	58	22.8	14	7	23	125
Ethyl acetate	71	9.7	39	20	67	150
Propyl acetate	102	3.3	300	150	500	170
Isopropyl acetate	90	6.3	150	75	250	165
Butyl acetate	126	1.0	1500	730	2400	95
Isobutyl acetate	115	1.9	880	440	1500	90
t-Butylacetate	98	-	330	160	530	185
Methoxyethanol	125	0.8	9.6	5	17	120
Ethoxyethanol	136	0.51	150	75	200	250
Methoxyethyl acetate	145	0.27	1700	860	2900	250
Ethoxyethyl acetate	156	0.16	8100	4000	1.3×10^4	250
Ketones						
Acetone	56	24.6	2.9	1.5*	5	120
Methyl ethyl ketone	80	10.3	21	11	35	145
Methyl isobutyl ketone	118	0.8	490	250	830	190

Organic compound	Boiling point (°C)	Vapour pressure kPa (25°C)	Retention volume (l)	SSV [a] (l)	SSV per gram (l.g^{-1})	Desorption Temperature (°C)
Alcohols						
Ethanol	78	5.9	2.4	1.2*	4	100
n-Propanol	97	1.9	17	8	27	125
Isopropanol	82	4.3	8.8	4.4	15	120
n-Butanol	118	0.67	96	50	170	155
Isobutanol	108	1.6	60	30	100	150
Others						
Ethylene oxide b	11	147	0.84	0.43	1.4	100
Propylene oxide	34	59	2.0	1.0	3.4	120
Hexanal	131	-	1680	840	2800	220

[a] reduce SSV by a factor of 2 if sampling at high humidity, see Appendix 1

* SSV below recommended 2.5 litres

Table 4 Diffusive uptake rates on sorbent tubes

Compound	Sorbent	Validation Level [a]	Uptake rate[b]	
			cm³ min⁻¹	ng ppm⁻¹ min⁻¹
Hydrocarbons				
n-Pentane	Chromosorb 106	A	0,50	1,46
	Carbopack B[c]	B	0,60	1,77
n-Hexane	Chromosorb 106	A	0,50	1,77
Benzene	Tenax TA[d]	A	0,41	1,3
	Porapak Q	A	0,42	1,37
	Tenax GR	B	0,57	1,81
	Chromosorb 106[e]	B	0,54	1,72
n-Heptane	Chromosorb 106	A	0,48	1,95
	Tenax TA[e]	A	0,43	1,77
	Carbotrap B	B	0,47	1,94
Toluene	Tenax TA[e]	B	0,44	1,67
	Tenax GR	B	0,56	2,12
	Chromosorb 106	B	0,52	1,94
	Carbopack B	B	0,55	2,06
n-Octane	Chromosorb 106	A	0,46	2,13
	Tenax TA[e]	A	0,43	2,00
Xylene	Tenax TA[e]	B	0,42	1,82
	Chromosorb 106	B	0,48	2,10
	Tenax GR	B	0,57	2,48
Ethylbenzene	Tenax TA[e]	B	0,46	2,0
	Tenax GR	B	0,56	2,43
	Chromosorb 106	B	0,44	1,9
	Porapak Q	D	0,55	2,38
Styrene	Tenax TA[e]	A	0,47	2,0
	Chromosorb 106	B	0,51	2,15
n-Nonane	Chromosorb 106	A	0,46	2,40
	Tenax TA[e]	A	0,40	2,12
Isopropylbenzene	Chromosorb 106	C	0,46	2,26
	Tenax TA[e]	C	0,46	2,26
	Porapak Q	D	0,51	2,5
Trimethylbenzene	Chromosorb 106	C	0,48	2,37
	Tenax TA[e]	C	0,48	2,37
n-Decane	Tenax TA	A	0,40	2,3
Halogenated hydrocarbons				
Methyl chloride	Spherocarb	B	0,63	1,3
Vinyl chloride	Spherocarb	B	0,78	2,0
1,1-Dichloroethene	Spherocarb	B	0,63	2,5

Compound	Sorbent	Validation Level [a]	Uptake rate[b]	
			cm^3 min^{-1}	ng ppm^{-1} min^{-1}
Trichlorotrifluoroethane	Chromosorb 102	B	0,46	3,5
Chlorotrifluoromethane	Chromosorb 102	B	0,42	1,8
Dichloromethane	Chromosorb 106	B	0,43	1,56
	Chromosorb 102	B	0,45	1,56
1,2-Dichloroethane	Chromosorb 102	B	0,47	1,9
Halothane	Tenax TA	B	0,32	2,59
	Chromosorb 102	B	0,45	3,6
Enflurane	Tenax TA	B	0,33	2,29
Isoflurane	Tenax TA	B	0,32	2,20
Bromoethane	Chromosorb 106	E	0,55	2,45
Trichloromethane (chloroform)	Tenax GR	B	0,45	2,18
	Chromosorb 102	B	0,48	2,35
Tetrachloromethane	Tenax GR	B	0,59	3,72
	Chromosorb 102	B	0,48	2,87
Trichloroethane	Chromosorb 106	B	0,47	2,66
	Chromosorb 102	B	0,43	2,3
1,1,1-Trichloroethane	Chromosorb 106	B	0,42	2,3
	Chromosorb 102	B	0,42	2,3
	Tenax GR	B	0,54	2,92
Tetrachloroethene	Chromosorb 106	B	0,46	3,1
	Tenax TA	B	0,41	2,8
	Chromosorb 102	B	0,38	2,6
Epichlorohydrin	Chromosorb 106	E	0,65	2,45
Perfluorodimethylcyclobutaned	Carbotrap	B	0,25	
Perfluoromethylcyclopentaned	Carbotrap	B	0,25	
Perfluoromethylcyclohexaned	Carbotrap	B	0,25	
Esters and glycol ethers				
Ethylacetate	Chromosorb 106[e]	B	0,49	2,00
	Tenax TA	B	0,40	1,60
n-Butylacetate	Tenax TA	B	0,61	2,26
Methyl methacrylate	Porapak Q	B	0,49	2,0
Butyl acrylate	Tenax TA	B	0,51	2,6
2-Methoxyethanol	Porapak Q	A	0,48	1,5
	Chromosorb 106	B	0,51	2,1
2-Ethoxyethanol	Tenax	A	0,44	1,8
2-Methoxyethyl acetate	Porapak Q	A	0,58	2,8
2-Ethoxyethyl acetate	Chromosorb 106	B	0,39	2,3
	Tenax TA	B	0,36	2,10
2-Butoxyethanol	Chromosorb 106	B	0,35	2,1
	Tenax TA	B	0,31	1,9

Compound	Sorbent	Validation Level [a]	Uptake rate[b]	
			cm³ min⁻¹	ng ppm⁻¹ min⁻¹
2-Methoxypropanol	Chromosorb 106[e]	B	0,45	1,85
	Tenax TA	B	0,37	1,52
2-Butoxyethyl acetate	Tenax	A	0,38	2,8
Aldehydes and ketones				
Methyl isobutyl ketone (2-methyl-4-pentanone)	Tenax TA	B	0,42	1,71
	Chromosorb 106[e]	B	0,49	2,01
Cyclohexanone	Tenax TA	D	0,57	2,3
Furfural	Tenax TA	A	0,63	2,5
Alcohols				
Propan-2-ol (isopropanol)	Spherocarb	C	0,81	2,0
Miscellaneous				
Acrylonitrile	Porapak N	A	0,62	1,35
Acetonitrile	Porapak N	A	0,60	1,0 (2 h)
	Porapak N	A	0,48	0,8 (8 h)
Propionitrile	Porapak N	A	0,53	1,4 (2 h)
	Porapak N	A	0,49	1,3 (8 h)
Carbon disulfide	Spherocarb	A	0,83	2,6
Nitrous oxide	Molecular Sieve 5A	B	0,70	1,25
Ethylene oxide	Spherocarb	B	0,88	1,6
1,4-Dioxane	Spherocarb	C	0,84	3,0

[a] Level A = validation equivalent to EN 838[11] level 1A
Level B = partial validation equivalent to EN 482[12]
Level C = calculated: ideal value
Level D = calculated from dynamic breakthrough volume
Level E = calculated from sorption isotherm
[b] Unless specified, values are for 4 h to 8 h exposures for workplace applications
[c] An example of sorbent type not recommended because of varying uptake rate
[d] Use nickel gauze instead of stainless steel gauze
[e] Preferred sorbent type

Table 6 Precision and storage recovery of volatile organic compounds on Tenax TA tubes

Organic compound	Loading µg	Times = 0 % CV[a]	Times = 5 months Mean recovery + % CV[b]		Times = 11 months Mean recovery + % CV	
			Recovery	Precision	Recovery	Precision
Hydrocarbons						
Hexane	7.8	10.7	93.6	17.9	100.8	26.1
Heptane	8.4	2.4	99.5	2.1	100.0	1.3
Octane	8.6	2.4	100.1	1.8	100.0	0.5
Nonane	12.0	0.8	-	-	101.0	0.4
Decane	9.2	2.2	100.4	1.5	100.2	0.5
Undecane	9.1	2.3	100.7	1.5	100.2	0.2
Dodecane	9.9	2.8	101.8	1.5	101.5	0.4
Benzene	11.0	2.5	98.7	2.0	98.6	0.8
Toluene	10.9	2.6	(100)	1.8	(100)	0.6
p-Xylene	5.3	2.5	99.9	1.7	99.8	0.7
o-Xylene	11.0	2.4	100.0	1.7	98.8	0.6
Ethylbenzene	10.0	0.5	99.6	0.4	97.9	1.3
Propylbenzene	10.5	2.3	99.7	1.5	98.5	0.7
Isopropylbenzene	10.9	2.3	98.9	1.8	97.2	1.3
m + p Ethyltoluene	10.5	2.3	98.8	1.7	96.9	1.2
o-Ethyltoluene	5.4	2.2	99.2	1.6	97.6	0.8
1,2,4-Trimethylbenzene	10.8	2.2	100.1	1.3	98.9	0.7
1,3,5-Trimethylbenzene	10.7	2.2	100.0	1.5	99.1	0.5
Trimethybenzene	10.2	1.7	101.6	0.5	101.3	0.8
Esters & glycolethers						
Ethyl acetate	10.3	0.6	97.6	1.0	100.0	2.5
Propyl acetate	10.9	2.4	100.5	1.7	99.1	0.8
Isopropyl acetate	9.4	1.0	97.0	0.4	100.0	1.4
Butyl acetate	10.8	2.4	100.3	1.6	99.9	0.6
Isobutyl acetate	10.7	2.3	100.2	1.4	99.8	0.7
Methoxyethanol	8.9	5.4	87.3	5.7	93.1	1.6
Ethoxyethanol	10.4	4.2	97.6	2.5	97.2	3.3
Butoxyethanol	10.0	2.6	100.6	4.1	100.1	3.0
Methoxypropanol	10.4	2.4	95.3	3.6	99.0	1.2
Methoxyethyl acetate	12.5	2.1	100.6	1.4	98.9	1.4
Ethoxyethyl acetate	11.4	0.9	99.8	2.2	98.7	2.6
Butoxyethylacetate	11.5	2.3	101.3	1.3	99.9	1.1
Aldehydes & Ketones						
Acetone	Not recommended on Tenax					
Methyl ethyl ketone	9.2	0.9	97.4	0.8	99.1	0.6
Methyl isobutyl ketone	9.3	0.6	100.7	0.6	100.7	0.5

Table 5 Sorbent tubes for Method 3 (pumped sampling and solvent desorption)

Organic compound	Sorbent	Organic compound	Sorbent
Acetic acid	Charcoal	Ketones	Charcoal
Acetonitrile	Charcoal	Methanol/ethanol	Silica gel
Aliphatic amines	Silica gel	Naphthas	Charcoal
Aliphatic hydrocarbons	Charcoal	Nicotine	XAD-7
Alcohols	Charcoal	Nitroaromatics	Silica gel
Aromatic amines	Silica gel	Nitroglycerin	Tenax
Aromatic hydrocarbons	Charcoal	Phenols/cresols	XAD-7
Butadiene	Charcoal	Phthalates	Tenax
Chlorinated hydrocarbons	Charcoal	Terpenes	Charcoal
Esters/glycol ethers	Charcoal	Turpentine	Charcoal

Organic compound	Loading µg	Times = 0 % CV[a]	Times = 5 months Mean recovery + % CV[b]		Times = 11 months Mean recovery + % CV	
Cyclohexanone	10.9	0.8	102.4	1.2	100.7	0.6
2-methylcyclohexanone	10.7	0.7	101.1	0.5	101.1	1.3
3-methylcyclohexanone	10.5	0.8	103.6	1.0	103.0	0.7
4-methylcyclohexanone	10.6	0.9	103.6	1.4	102.7	0.6
3,5,5-trimethylcyclohex-2-enone	10.6	2.3	101.4	0.9	97.7	1.2
Alcohols						
Isopropanol	Not recommended on Tenax					
n-Butanol	9.0	1.1	94.8	3.0	96.9	1.2
Isobutanol	8.9	1.0	93.6	3.5	96.4	1.0
Chlorinated Hydrocarbons						
Epichlorohydrin	20	5.5	99.3*	1.9	107.5**	2.4

[a] 6 replicates
[b] Normalised to toluene = 100. The stability of toluene has been established in a BCR intercomparison[10]
* Storage for 1 week
** Storage for 4 weeks

References

1   *General methods for sampling and gravimetric analysis of respirable, thoracic and inhalable aerosols* MDHS14/4 HSE 2014
www.hse.gov.uk/pubns/mdhs/index.htm

2   BS EN ISO 16017-1:2001 *Indoor, ambient and workplace air. Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography: Part 1: Pumped sampling* British Standards Institution

3   BS EN ISO 16017-2:2003 *Indoor, ambient and workplace air. Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography: Part 2: Diffusive sampling* British Standards Institution

4   BS ISO 16200-1:2001 *Workplace air quality. Sampling and analysis of volatile organic compounds by solvent desorption/gas chromatography: Part 1: Pumped sampling method* British Standards Institution

5   US Occupational Safety and Health Administration *OSHA Manual of analytical methods* USDOL/OSHA 1989, plus updates

6   *NIOSH Manual of Analytical Methods* (Fourth edition) 1994, US Dept of Health and Human Services, Publication 94-113, plus updates

7   BS EN ISO 13137:2013 *Workplace atmospheres: Pumps for personal sampling of chemical and biological agents. Requirements and test methods* British Standards Institution

8   BS EN ISO 1042:2000 *Laboratory glassware: One-mark volumetric flasks* British Standards Institution

9   BS EN ISO 8655-6:2002 *Piston operated volumetric apparatus. Gravimetric methods for the determination of measurement error* British Standards Institution

10   Brown R H and Purnell C J 'Collection and analysis of trace organic vapour pollutants in ambient atmospheres. The performance of a Tenax-GC adsorbent tube' *J Chrom* 178 1979 79-90

11   EN 838 *Workplace atmospheres: Diffusive samplers for the determination of concentrations of gases and vapours – Requirements and test methods*

12   BS EN 482:2012 *Workplace exposure. General requirements for the performance of procedures for the measurement of chemical agents* British Standards Institution

13   *Study of sorbing agents for the sampling of volatile compounds from air* EC Contract MAT1-CT92-0038 Final Report (1995)

14   BS EN 1076:1997 *Workplace atmospheres. Pumped sorbent tubes for the determination of gases and vapours – Requirements and test methods* British Standards Institution

15   ISO 5725-1:1994 *Accuracy (trueness and precision) of measurement methods and results – Part 1: general principles and definitions*

16   Coker D T et al *A monitoring method for gasoline vapour giving detailed composition Ann Occup Hyg 1989* **33** 15-26

17   Wright M D *Diffusive uptake rates for the Perkin Elmer tube —* BCR air sampling intercomparison at Vito. Mol, Belgium Feb 1991 – April 1992. HSE internal report 1993 IR/L/IA/93/3 Health and Safety Laboratory

18   Plant NT Wright M D *European Diffusive Sampling Initiative: Project report with status at March* 1998 IACS 98/01 Health and Safety Laboratory

19   Taylor DG Kupel RE Bryant JM *Documentation of the NIOSH Validation Tests* NIOSH Cincinnati, OH, USA, 1977

You should use the current edition of any standards listed.

Further information

For information about health and safety, or to report inconsistencies or inaccuracies in this guidance, visit www.hse.gov.uk/. You can view HSE guidance online and order priced publications from the website. HSE priced publications are also available from bookshops.

This MDHS is available at: www.hse.gov.uk/pubns/mdhs/index.htm.

For further information about this method or other MDHS methods, please visit HSL's website: www.hsl.gov.uk or email: hslinfo@hsl.gov.uk