MDHS

Methods for the Determination of
Hazardous Substances
Health and Safety Laboratory

HSE
Health & Safety
Executive

80

Volatile organic compounds in air

Laboratory method using diffusive solid sorbent tubes, thermal desorption and gas chromatography

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INTRODUCTION

Requirements of the COSHH Regulations

1 The Control of Substances Hazardous to Health (COSHH) Regulations[1] require that persons who may be exposed to substances hazardous to health receive suitable and sufficient information, instruction and training. The COSHH Regulations also include a requirement to assess the health risk created by work involving substances hazardous to health, and to prevent or control exposure to such substances. Employers must therefore ensure that the requirements of the COSHH Regulations are fully satisfied before allowing employees to undertake any procedure described in this method.

Analytical methods

2 A number of analytical methods are available for the determination of volatile organic compounds in air, including other methods in the MDHS series[2] for individual compounds and for hydrocarbon mixtures. The use of methods not included in the MDHS series is acceptable provided they have the accuracy and reliability appropriate to the application.

Quality control

3 An appropriate level of quality control should be employed when using this method. Guidance is given in MDHS 71.[3] The long-term stability (paragraph 15) of volatile organic compounds (paragraph 16) on Tenax is good. The stability of these compounds on Chromosorb 106 or the other sorbents (paragraphs 21-23) is not known, but is expected to be good on the basis of the tests with Tenax. If a standard operating procedure is used, analysis of an internal quality control sample (at say 1 mg loading) can be used as a quality check on the basis of a working standard deviation of 3.6% (warning at ± 2SD; action at ± 3SD). It is strongly advised that analysts participate in an external quality control scheme. A satisfactory performance in WASP (which includes an analysis of aromatic hydrocarbons on thermal desorption tubes) would give added confidence in performing this method.

PRINCIPLE

4 An appropriate sorbent is selected for the compound or mixture to be sampled (more than one tube may be necessary, but sorbents should not be mixed in the same tube). The rate of sampling is determined by prior calibration in a standard atmosphere (paragraphs 11 and 52). The diffusive sampler is exposed to air for a measured time period. The organic compound vapour(s) migrate down the tube by diffusion and are collected on the sorbent. The collected vapour(s) are desorbed by heat and are transferred under inert carrier gas into a gas chromatograph equipped with a suitable capillary column and a flame ionisation detector (paragraphs 27 and 28), where they are analysed.

SCOPE AND FIELD OF APPLICATION

5 This method specifies a sorbent tube/gas chromatographic method for the determination of the time-weighted average concentrations of volatile organic compounds in workplace air. The method is suitable for the measurement of the airborne concentrations of individual compounds and of components of volatile organic mixtures.

6 This method recommends a number of different sorbents for use in the sample tube, which are appropriate for different ranges of volatile organic compounds. For example, Tenax is appropriate for aliphatic hydrocarbons from C7 (heptane) to C10 (decane) and aromatic compounds from toluene to cumene. It is also suitable for

esters, ketones, chlorinated hydrocarbons, alcohols and ethers of similar volatilities. It is suitable for higher boiling compounds, provided they can be efficiently desorbed at the temperatures available on the thermal desorption apparatus used, but more volatile materials must be sampled on stronger sorbents, such as Porapak, Chromosorb, Spherocarb or charcoal. Sorbents other than those specified may be used if their diffusive uptake rates (paragraph 11) are known and their thermal desorption blanks (paragraph 24) are sufficiently small.

7 The method is valid for the measurement of airborne vapours of these volatile organic compounds in a concentration range of approximately 1 to 1000 mg/m^3 individual organic for exposure times between 30 min and 8 h. The upper limit of the useful range is set 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 on the detector and on blank levels of analyte on the sorbent tubes.

8 This procedure can be used for personal and fixed location sampling. It cannot be used to measure instantaneous or short-term fluctuations in concentration. Alternative on-site procedures, such as gas chromatography, infrared spectrometry or a total organic analyser, shall be used to monitor rapidly changing concentrations of single substances or mixtures.

Interferences

9 Organic components which 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 proper selection of gas chromatographic columns and conditions. The method is suitable for use in atmospheres of up to 95% relative humidity.

Precision and accuracy

10 The method has been examined, in accordance with a diffusive sampler evaluation protocol,[4,5] using a Perkin-Elmer diffusive tube containing an appropriate sorbent. There was no silicone membrane in the diffusion cap. The results of this evaluation are given in a variety of sources and are summarised in *The Diffusive Monitor.*[6] Different uptake rates may be given by other makes of diffusive tube, or if a membrane is employed, or if a different adsorbent is used, but the general performance of other systems is expected to be similar to that described here (see paragraphs 11 and 52).

Uptake rates

11 The diffusive uptake rates for typical organic vapours on a variety of sorbents are given in Table 1. This list has been compiled from sources available to the Health and Safety Laboratory and is not complete. The original source references are given in *The Diffusive Monitor* and users of the data are strongly advised to consult these to determine the level of confidence and range of applicability of the values. Approximate values for diffusive uptake rates that are not listed may be obtained by using the empirical relationship between U_{ratio} and V_g.[7] U_{ratio} is the effective uptake rate U_{eff} divided by the theoretical uptake rate U_{th}. V_g is the dynamic specific retention volume.

12 The random error of the determination of concentrations of volatile organic compounds in air by this method, ie the precision of the laboratory determination of the uptake rate values given in paragraph 11, is about 12%, expressed as a coefficient of variation. This value is based on data obtained for benzene, toluene, heptane, xylene and decane.[8]

13 The uptake rate of the sampler is not significantly affected by ambient air movement, provided a minimum of about 0.01 m s^{-1} is maintained. It is not significantly affected by exposure of the sampler alternately to test atmosphere and clean air for 16 h, provided an appropriate sorbent is used.

14 There is a slight reduction in the uptake rate of the sampler for benzene with increasing ambient temperature, amounting to about 0.0008 cm^3 min^{-1} (°C)$^{-1}$ or 0.2% (°C)$^{-1}$. A similar change in uptake rate with temperature is expected for other compounds. The sampling rate is unaffected by humidity up to 95% rh at 20°C. The sampling rate of toluene is unaffected by the simultaneous presence of hexane, heptane, decane and xylene.[7]

Storage

15 Laboratory tests on tubes spiked with the compounds specified in paragraph 16 at a single load level of approximately 10 µg and stored at room temperature for 5 months are summarised in Table 2. Excluding hexane and methoxyethanol, the mean recovery (relative to unstored tubes) was 99.7% and the mean RSD_r was 2%. Similar results were obtained after storage for 11 months; excluding hexane and methoxyethanol, the mean recovery (relative to unstored tubes) was 99.4% and the mean RSD_r was 0.9%.

Note Precision and related terms: repeatability r, reproducibility R, repeatability relative standard deviation RSD_r, reproducibility relative standard deviation RSD_R and bias are defined as in ISO 5725[9] or IUPAC.[10]

16 The method is suitable for a range of volatile organic compounds, either singly or in mixture, and the chromatograph should be calibrated with the compound or compounds of interest. Three organic solvent mixtures are given as examples, which are arranged to give resolved peaks on both BP-1 and BP-10 columns; other mixtures may be more appropriate on other columns.

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

Mixture 2 consists of: iso-propanol, iso-butanol, n-butanol, ethoxyethanol, methoxyethanol, propylene glycol monomethyl ether, butoxyethanol, 1,2,3-trimethylbenzene, ethylbenzene, ethyl acetate, ethoxyethyl acetate, toluene.

Mixture 3 consists of: acetone, 2-butanone, methyl isobutyl ketone, cyclohexanone, 2-methylcyclohexanone, 3-methylcyclohexanone, 4-methylcyclohexanone, iso-propyl acetate, isophorone, n-nonane, toluene.

Methanol

17 This should be of chromatographic quality. It must be free from compounds co-eluting with the compound or compounds of interest (paragraph 13).

Sorbent

18 One or more of the following, or equivalent.

Tenax

19 A porous polymer sorbent (Tenax or equivalent), particle size 0.18-0.25 mm (60-80 mesh) should be used. (Tenax is a registered trademark of the Akzo Research Co.) The sorbent should be preconditioned by heating in an inert atmosphere at 250°C for 16 h before packing the tubes. To prevent recontamination of the sorbent, it shall be kept in a clean atmosphere during its cooling to room temperature, storage, and loading into the tubes. Tenax is available in a number of forms, including Tenax TA and Tenax GR (graphitised).

Chromosorb

20 A porous polymer sorbent (Chromosorb or equivalent), particle size 0.18-0.25 mm (60-80 mesh) should be used. (Chromosorb is a registered trademark of the Johns Mannville Co.) The sorbent should be preconditioned by heating in an inert atmosphere at 190°C for 16 h before packing the tubes. To prevent recontamination of the sorbent, it shall be kept in a clean atmosphere during its cooling to room temperature, storage, and loading into the tubes. Chromosorb is available in a number of forms, including Chromosorb 102 and 106. Chromosorb 106 may be conditioned at 250°C.

Porapak

21 A porous polymer sorbent (Porapak or equivalent), particle size 0.18-0.25 mm (60-80 mesh) should be used. (Porapak is a registered trademark of Waters Associates Co.) The sorbent should be preconditioned by heating in an inert atmosphere at 180°C for 16 h before packing the tubes. To prevent recontamination of the sorbent, it shall be kept in a clean atmosphere during its cooling to room temperature, storage, and loading into the tubes. Porapak is available is a number of forms, including Porapak Q and Porapak N.

Spherocarb

22 A porous polymer sorbent (Spherocarb or equivalent), particle size 0.18-0.25 mm (60-80 mesh) should be used. (Spherocarb is a registered trademark of Foxboro Analytical Co.) The sorbent should be preconditioned by heating in an inert atmosphere at 300°C for 16 h before packing the tubes. To prevent recontamination of the sorbent, it shall be kept in a clean atmosphere during its cooling to room temperature, storage, and loading into the tubes.

Activated charcoal

23 Activated charcoal (acid-washed Sutcliffe Speakman 607C or equivalent), particle size 0.18-0.25 mm (60-80 mesh) should be used. The charcoal should be preconditioned by heating in an inert atmosphere at 250°C for 16 h before packing the sorbent tubes. To prevent recontamination of the charcoal, it shall be kept in a clean atmosphere during its cooling to room temperature, storage, and loading into the tubes.

APPARATUS

Ordinary laboratory apparatus and

Sorbent tubes

24 Sorbent tubes should be compatible with the thermal desorption apparatus to be used (paragraph 25). Typically, but not exclusively, they are constructed of stainless steel tubing, 6.3 mm OD, 5 mm ID and 90 mm long. One end of the tube is marked, for example by a scored ring about 10 mm from the end. The tubes are packed with preconditioned sorbent (paragraph 18) so that the sorbent bed will be within the desorber heated zone. Tubes contain typically about 200 mg porous polymer or 300 mg charcoal. The sorbents are retained by stainless steel gauzes and/or silanised glass wool plugs. Prior to use, tubes should be conditioned by heating slowly under inert carrier gas to the conditioning temperature (paragraphs 19-23) and maintaining that temperature for 10 min. Tubes should then be analysed to ensure that the thermal desorption blank is sufficiently small. If the blank is unacceptable, tubes should be reconditioned. Once a sample has been analysed, it may be reused for a further sample immediately. However, it is advisable to check the thermal desorption blank if the tubes are left for an extended period before reuse, or if sampling for a different analyte is envisaged. Tubes should be sealed and stored in an airtight container when not sampling or being conditioned.

Note The sorbent tube blank level is acceptable if it is no greater than the equivalent of 10 ng for any of the calibration compounds (paragraph 16). Typical levels are much less than this.

Thermal desorption apparatus

25 Apparatus for the two-stage thermal desorption of the sorbent tubes and transfer of the desorbed vapours via an inert gas flow into a gas chromatograph will be required. A typical apparatus contains a mechanism for holding the tubes to be desorbed while they are heated and purged simultaneously with inert carrier gas. The desorption

temperature and time are adjustable, as is the carrier gas flow rate. The desorbed sample, contained in the purge gas, is routed to the gas chromatograph via a heated transfer line. Some types of apparatus incorporate additional features, such as automatic sample tube loading, leak-testing, and a cold trap in the transfer line to concentrate the desorbed sample.

26 Two types of end cap should be available. One type, used for sealing the tubes when they are stored, is a closed metal end cap with PTFE or Viton seals. The other, diffusive, end cap should be similar but should allow the ingress of vapour through a metal gauze, the size of the opening being the same as the cross-section of the tube. Some versions of the diffusive end cap incorporate a silicone membrane next to the gauze.

Gas chromatograph

27 A gas chromatograph fitted with a flame ionisation detector, capable of detecting an injection of 5 ng toluene with a signal-to-noise ratio of at least 5 to 1.

28 A gas chromatograph column capable of separating the analytes of interest from other components. A 50 m dimethylsiloxane (eg BP-1) or a 50 m 7% cyanopropyl, 7% phenyl, 86% methyl siloxane (eg BP-10) glass capillary column has been found suitable for this analysis[11] (paragraph 43).

Injection facility for preparing standards

29 A conventional gas chromatographic injection port may be used for preparing sample tube standards. This can be used in situ, or it can be mounted separately. The carrier gas line to the injector should be retained. The back of the injection port should be adapted if necessary to fit the sample tube. This can be done conveniently by means of a compression coupling with a Viton O-ring seal.

Collection of samples

30 Select a sorbent tube (more than one may be necessary) appropriate for the compound or mixture to be sampled. Guidance on suitable sorbents is given in Table 1. Immediately before sampling, remove the end cap from the marked end of the sample tube and replace it with a diffusion end cap. Make sure the diffusion cap is properly seated and the other end cap is in place.

31 When used for personal sampling, the tube should be mounted in the worker's breathing zone, for example on a lapel. The orientation of the tube is not critical. When used for fixed location sampling, a suitable sampling site is chosen. However, if outdoors or otherwise exposed to rain, expose the tube with the closed end uppermost to avoid collection of rainwater.

32 At the end of a measured period of exposure, remove the diffusion end cap and replace the closed cap. If the sample is not to be analysed immediately, store the sample in an airtight container, for example an aluminised plastic bag.

33 Sample blanks should be prepared by using tubes identical to those used for sampling and subjecting them to the same handling procedure as the sample tubes except for the actual period of sampling.

Blanks

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

Preparation of standard solutions

Calibration blend solution containing approximately 10 mg/ml each component.

35 Accurately weigh approximately 1 g of each of the substances in mixture 1 (paragraph 13) into a 100 ml volumetric flask, starting with the least volatile substance. Make up to 100 ml with methanol (paragraph 17), stopper and shake to mix.

Note Other specific volatile organic components may be included in the calibration blend by adding 1 g of the relevant component before making up to volume.

Prepare similar calibration solutions from mixtures 2 or 3 (paragraph 13) if required.

Calibration blend solution containing approximately 1 mg/ml of each component.

36 Introduce 50 ml of methanol into a 100 ml volumetric flask. Add 10 ml of solution 44. Make up to 100 ml with methanol, stopper and shake to mix.

Calibration blend control solution containing approximately 5 mg/ml of each component.

37 Accurately weigh approximately 0.5 g of each of the substances specified in paragraph 13 into a 100 ml volumetric flask, starting with the least volatile substance. Make up to 100 ml with methanol (paragraph 17), stopper and shake to mix.

Stability of calibration blend solutions

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

Standard loaded sorbent tubes

39 Loaded sorbent tubes are prepared by injecting aliquots of standard solutions onto clean sorbent tubes as follows. A sorbent tube is fitted into the injection unit (paragraph 29) through which inert purge gas is passed at 100 ml/min and a 1 to 4 µl aliquot of an appropriate standard solution injected through the septum. After 5 min, the tube is disconnected and sealed. Prepare fresh standards with each batch of samples. In this manner, load sorbent tubes with 4 µl, 2 µl and 1 µl of solution 35,

and 4µl, 2 µl and 1µl of solution 36. Also load sorbent tubes with 4 µl of control solution 37.

Desorption and analysis

40 The sorbent tube is placed in a compatible thermal desorption apparatus. Air is purged from the tube to avoid chromatographic artefacts arising from the thermal oxidation of the sorbent or gas chromatographic packing. The tube is then heated to displace the organic vapours which are passed to the gas chromatograph by means of a carrier gas stream. The gas flow at this stage should be the reverse of that used during sampling, ie the marked end of the tube should be nearest the gas chromatograph column inlet. While reversing the flow is not essential, it helps to ensure high desorption efficiency.

41 The desorbed sample occupies a volume of several millilitres of gas, so that it may need to be concentrated if good chromatographic peak shape and resolution are to be obtained. This may be achieved by using a secondary sorbent and/or a cold trap external to the gas chromatograph. Alternatively, the desorbed sample can be passed directly to the gas chromatograph where it is concentrated by holding the column initially at low temperature, typically about 10°C, or indirectly via a holding reservoir, from which it is subsampled before injection.

Desorption conditions should be chosen such that desorption from the sample tube is complete, and no sample loss occurs in the secondary trap, if used. Typical parameters are:

Desorb temp	250°C
Desorb time	5 min
Transfer line	150°C
Cold trap low	-30°C
Cold trap high	300°C
Cold trap sorbent	sorbent, 40 mg
Carrier gas	helium

43 Set up the gas chromatograph for the analysis of volatile organic compounds. A variety of chromatographic columns may be used for the analysis of these compounds. The choice will depend largely on which compounds, if any, are present that might interfere in the chromatographic analysis. Suitable choices are 50 m x 0.22 mm fused silica columns with thick-film BP-1 or BP-10 stationary phase. Typical operating conditions for this column are a temperature programme from 50 to 250°C at 5°C/min, with an initial hold time of 10 min at 10°C. Retention indices for the compounds in calibration solutions 16 are given in Table 3.

44 The capillary column should be threaded back through the transfer line from the thermal desorption apparatus to the gas chromatograph such that the capillary is 1-2 mm from the sorbent in the cold trap. The split valve is conveniently placed at the chromatograph end of the transfer line. A typical split ratio is 100:1.

45 Correspondence of retention time on a single column should not be regarded as proof of identity.

Calibration

46 Analyse each sorbent tube standard (paragraph 39) by thermal desorption and gas chromatography. Prepare a 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 mass of the analyte, in micrograms, in the injected aliquot of the calibration blend solutions

where

mass of analyte (µg) = concentration in solution 35 or 36 x volume injected (µl; section 39).

47 Check the calibration graph by analysing the independently prepared control solution 37 (standard tube 39). If the result does not agree with the previous calibration line within 10%, prepare fresh standards and carry out a new calibration.

Determination of sample concentration

48 Analyse the samples and sample blanks as described for the calibration standards in paragraph 46. Determine the peak response and read from the calibration graph the mass of the analyte in the desorbed sample.

Determination of desorption efficiency

49 The efficiency of desorption should be checked by injecting aliquots of the standard solutions directly into the gas chromatograph. Prepare a second calibration graph of peak area against mass of analyte as in paragraph 46. This calibration should be the same or nearly the same as that in the first graph. The desorption efficiency is the response of a tube standard divided by that of the corresponding liquid standard injected directly. If the desorption efficiency is less than 95%, change the desorption parameters accordingly.

50 Some makes of thermal desorber do not have a direct liquid injection facility. In these cases, desorption efficiency should be checked by comparing the calibration graph of the substance of interest with that of n-heptane (mixture 1, paragraph 16). The ratio of the slope of the calibration graph of the substance of interest relative to that of n-heptane should be the same as the relative response factor for that compound. Typical response factors for the substances in paragraph 16 are given in Table 3. Response factors for other compounds may be calculated approximately from effective carbon numbers.[12] If the ratio of the slopes of the calibration graphs do not agree with the relative response factor within 10%, change the desorption parameters accordingly. Alternatively, check that the desorption efficiency is at least 95% by desorbing the standard loaded tubes (paragraph 39) a second time; the second desorption should give a peak response less than 5% of the first.

51 Ideally, desorption efficiencies should be determined on tube standards loaded from a standard atmosphere (MDHS 3 or 4)[2], as the method described may not take account of ambient conditions (eg humidity,

co-contaminants) prevailing during sampling. However, for thermal desorption, ambient conditions have little effect on desorption efficiencies, and the described method is much more convenient. It should be noted, however, that carbonaceous sorbents can collect a large amount of water in high humidity conditions, and this can affect split ratios with capillary columns on desorption.

Calibration of uptake rate

52 The uptake rates given in paragraph 11 are for tubes with dimensions as in paragraph 24 without a membrane. For other specifications it may be necessary to follow the protocol[4,5] to determine the relevant uptake rate and its range of applicability.

CALCULATIONS

Mass concentration of analyte

53 Calculate the weight, in μg, of organic vapour in the sample by using the calibration graph prepared for 'spiked' tube standards (paragraph 46). Also calculate the weights of organic vapour in the blank tubes (paragraph 34).

Then

$$\text{Concentration of organic vapour in air (mg m}^{-3}\text{)} = \frac{1000(m - m_{blank})}{U' \times t}$$

where

m = weight (μg) of organic vapour on sample tube
m_{blank} = weight (μg) of organic vapour on blank tube
U' = uptake rate (cm^3 min^{-1}; paragraph 11)
t = exposure time (min)

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

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

where:

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

Volume concentration of analyte

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

$$\text{Concentration of organic vapour in air (ppm)} = \frac{1000(m - m_{blank})}{U \times t}$$

where

U = uptake rate (ng ppm^{-1} min^{-1}; paragraph 11)

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

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

where

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

REPORT

56 The test report shall contain at least the following information:

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

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Table 1 Diffusive uptake rates on Perkin-Elmer sorbent tubes (without membrane)

Compound	*Sorbent*	*Level*	*Uptake rate*[1]	
			cm^3 min^{-1}	*ng ppm^{-1} min^{-1}*
Hydrocarbons				
1,3-butadiene	Molecular Sieve 13X	A	0.59	1.3
n-pentane	Chromosorb 106	A	0.5	1.46
	Carbopack B*	B	0.6	1.77
n-hexane	Chromosorb 106	A	0.5	1.77
benzene	Tenax TA[3]	A	0.41	1.3
	Porapak Q	A	0.42	1.37
	Tenax GR	B	0.57	1.81
	Chromosorb 106*	B	0.54	1.72
n-heptane	Chromosorb 106	A	0.48	1.95
	Tenax TA*	A	0.43	1.77
	Carbotrap B	B	0.47	1.94
toluene	Tenax TA*	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*	A	0.43	2.00
xylene	Tenax TA*	B	0.42	1.82
	Chromosorb 106	B	0.48	2.10
	Tenax GR	B	0.57	2.48
ethyl benzene	Tenax TA*	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*	A	0.47	2.0
	Chromosorb 106	B	0.51	2.15
n-nonane	Chromosorb 106	A	0.46	2.40
	Tenax TA*	A	0.4	2.12
isopropylbenzene	Chromosorb 106	C	0.46	2.26
	Tenax TA*	C	0.46	2.26
	Porapak Q	D	0.51	2.5
trimethylbenzene	Chromosorb 106	C	0.48	2.37
	Tenax TA*	C	0.48	2.37
n-decane	Tenax TA	A	0.4	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
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 (carbon tetrachloride)	Tenax GR	B	0.59	3.72
	Chromosorb 102	B	0.48	2.87
trichloroethene	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

Compound	*Sorbent*	*Level*	*Uptake rate*[1]	
			$cm^3\ min^{-1}$	$ng\ ppm^{-1}\ min^{-1}$
epichlorohydrin	Chromosorb 106	E	0.65	2.45
perfluorodimethyl-cyclobutane[4]	Carbotrap	B	0.25	
perfluoromethyl-cyclopentane[4]	Carbotrap	B	0.25	
perfluoromethyl-cyclohexane[4]	Carbotrap	B	0.25	
Esters and glycol ethers				
ethyl acetate	Chromosorb 106*	B	0.49	2.0
	Tenax TA	B	0.4	1.6
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	2.1
2-butoxyethanol	Chromosorb 106	B	0.35	2.1
	Tenax TA	B	0.31	1.9
2-methoxypropanol	Chromosorb 106*	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*	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[5]	A	0.62	1.35
acetonitrile	Porapak N[5]	A	0.6	1.0 (2 h)
	Porapak N[5]	A	0.48	0.8 (8 h)
propionitrile	Porapak N[5]	A	0.53	1.4 (2 h)
	Porapak N[5]	A	0.49	1.3 (8 h)
carbon disulphide	Spherocarb	A	0.83	2.6
nitrous oxide	Mol. Sieve 5A[5]	B	0.7	1.25
ethylene oxide	Spherocarb	B	0.88	1.6
1,4-dioxane	Spherocarb	C	0.84	3.0

Notes

1 Rates are given for tubes with dimensions as in paragraph 24 without a membrane. For other specifications, see the guidance in paragraph 10. Unless specified, values are for 4-8 h exposures.
2 Means preferred sorbent.
3 Sorbent not recommended because of varying uptake rate.
4 A nickel disk, rather than the conventional stainless steel gauze, was used to support the Carbotrap sorbent materials during method validation for these perfluorocarbon tracer gases. The uptake rates may not be applicable to samples using conventional steel gauzes.
5 Rate varies predictably with exposure dose.

Levels

Level A = validation equivalent to CEN level 1A[13]
Level B = partial validation - laboratory tests to CEN level 1B[13]
Level C = calculated - ideal value
Level D = calculated from dynamic breakthrough volume
Level E = calculated from sorption isotherm

* Preferred sorbent

Table 2 Precision and storage recovery of organic vapours on Tenax tubes

Organic compound	*Loading (µg) (time = 0)*	*%CV**	*mean recovery**+ %CV**			
			time = 5 months		*time = 11 months*	
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	0.5
nonane	12	0.8	n.d.	n.d.	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	2.5	98.7	2	98.6	0.8
toluene	10.9	2.6	(100.0)	1.8	(100.0)	0.6
p-xylene	5.3	2.5	99.9	1.7	99.8	0.7
o-xylene	11	2.4	100	1.7	98.8	0.6
ethylbenzene	10	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	1.5	99.1	0.5
trimethylbenzene	10.2	1.7	101.6	0.5	101.3	0.8
Chlorinated hydrocarbons						
epichlorohydrin	20	5.5	99.3***	1.9	107.5****	2.4
Esters and glycol ethers						
ethyl acetate	10.3	0.6	97.6	1	100	2.5
propyl acetate	10.9	2.4	100.5	1.7	99.1	0.8
isopropyl acetate	9.4	1	97	0.4	100	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	2.6	100.6	4.1	100.1	3
methoxypropanol	10.4	2.4	95.3	3.6	99	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
butoxyethyl acetate	11.5	2.3	101.3	1.3	99.9	1.1
Aldehydes and 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
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	103	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					
butanol	9	1.1	94.8	3	96.9	1.2
isobutanol	8.9	1	93.6	3.5	96.4	1

* 6 replicates

** normalised to toluene = 100. The stability of toluene has been established in a BCR intercomparison[13]

*** Storage for one week

**** Storage for four weeks

Table 3 Identification of components on BP-1 and BP-10 capillary columns operated as specified in paragraph 43. Temperature-programmed retention indices are included as a guide only.

	Retention index		*Response factor*
	BP-1	*BP-10*	
Calibration mix 1			
toluene	762	826	1.07
o-xylene	887	961	1.02
p-xylene	864	929	1
isopropylbenzene	919	983	0.97
o-ethyltoluene	975	1047	1.02
m-ethyltoluene	956	1022	1.01
p-ethyltoluene	958	1023	1
1,2,4-trimethylbenzene	990	1060	0.97
1,3,5-trimethylbenzene	964	1029	0.98
n-propyl acetate	695	784	n.d.
n-butyl acetate	795	883	0.55
iso-butyl acetate	756	840	0.54
methoxyethyl acetate	807	941	n.d.
butoxyethyl acetate	1061	1185	n.d.
benzene	652	724	1.12
n-propylbenzene	949	1015	1.01
Calibration mix 2			
isopropanol	527	597	0.53
n-butanol	644	776	0.6
iso-butanol	610	738	0.68
methoxyethanol	616	754	n.d.
ethoxyethanol	696	821	0.45
propylene glycol monomethyl ether	658	776	n.d.
butoxyethanol	890	1016	0.62
1,2,3-trimethylbenzene	1019	1098	0.98
ethylbenzene	855	922	1.03
ethyl acetate	598	680	0.38
ethoxyethyl acetate	877	1002	0.5
Calibration mix 3			
acetone	524	594	0.49
2-butanone	582	693	0.61
cyclohexanone	872	1030	0.72
2-methylcyclohexanone	930	1073	n.d.
3-methylcyclohexanone	932	1088	n.d.
4-methylcyclohexanone	938	1095	n.d.
isopropyl acetate	643	727	0.49
isophorone	1107	1298	0.85

TITLES IN THE MDHS SERIES

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