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Occupational Medicine and Hygiene Laboratory

MDHS 72

Methods for the Determination of Hazardous Substances

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Volatile organic compounds in air

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

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 for individual compounds and for hydrocarbon mixtures other methods in the MDHS series.[2] 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 of volatile organic compounds (paragraph 13) is good (paragraph 12). The stability of these compounds on Chromosorb 106 or the other sorbents (paragraph 18) 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 µg 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 A measured volume of sample air is drawn through one (or more) sorbent tubes in series, an appropriate sorbent (or sorbents) being selected for the compound or mixture to be sampled. Provided suitable sorbents are chosen, volatile organic components are retained by the sorbent tube and thus are removed from the flowing air stream. The collected vapour (on each tube) is desorbed by heat and is transferred under inert carrier gas into a gas chromatograph equipped with a suitable capillary column and a flame ionization detector (paragraphs 32 and 33), where it is 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 C_6 (hexane) to C_{10} (decane) and aromatic compounds from benzene 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. Other sorbents than those specified may be used if their breakthrough capacities (paragraph 42) are adequate 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 0.2 to 100 mg/m^3 individual organic for samples of 2.5 litres of air. 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 sorptive capacity is measured as a breakthrough volume of air, which determines the maximum air volume that must not be exceeded when sampling. The lower limit of the useful range depends on the noise level on the detector and by blank levels of analyte on the sorbent tubes.

8 This procedure is compatible with low flow rate personal sampling pumps and 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, should 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

10 Laboratory tests of a similar procedure,[4] using tubes spiked with some of the compounds specified in paragraph 13 (n-pentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, benzene, toluene, o-xylene, isopropylbenzene) at levels in the range 0.5 to 500 μg each compound, indicated a mean repeatability relative standard deviation (RSD) of 5%. The reproducibility RSD was 12%. Assuming a pump error of 5%, the combined sampling and analytical errors are 7% and 13% respectively. In a second trial, using tubes spiked with a larger range of analytes, including propane and butane isomers, from a standard atmosphere, mean repeatability and reproducibility, including pump errors, were 12% and 26% respectively.

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[5] or IUPAC.[6]

11 Laboratory tests on tubes spiked with the compounds specified in paragraph 13 at a single load level of approximately 10 μg are summarised in Table 1. Excluding hexane, the mean RSD_r was 2%. The bias of the method is expected to be better than 5%.

Storage

12 Laboratory tests on tubes spiked with the compounds specified in paragraph 13 at a single load level of approximately 10 μg and stored at room temperature for 5 months are summarised in Table 1. 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%.

REAGENTS

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

Volatile organic compounds

13 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.

Notes

(1) Benzene is a recognised human carcinogen. Avoid any exposure by inhalation or skin contact.

(2) n-Hexane presents a serious health hazard if incorrectly handled. Avoid any exposure by inhalation or skin contact.

Mixture 1

14 These components are:

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-butylacetate, iso-butyl acetate, methoxyethyl acetate, butoxyethyl acetate.

Mixture 2

15 These components are:

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

16 These components are:

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 preconditioned by heating in an inert atmosphere at 250°C for 16 hr before packing the tubes. To prevent recontamination of the sorbent, it should be kept in a clean atmosphere during its cooling to room temperature, storage, and loading into the tubes.

Chromosorb 106

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

Porapak N

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

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 hr before packing the tubes. To prevent recontamination of the sorbent, it should 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 hr before packing the sorbent tubes. To prevent recontamination of the charcoal, it should 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 These 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 (¼ inch) 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 silanized glass wool plugs. Prior to use, tubes should be conditioned by heating slowly under inert carrier gas to 250°C (180°C for Porapak N) 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 100 ng for any of the calibration compounds (paragraph 13). 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.

Sorbent tube end caps

26 The tubes are sealed with metal fittings with PTFE seals.

Sorbent tube unions

27 Two sorbent tubes may be connected in series during sampling with metal fittings with PTFE seals.

Precision syringe

28 A precision syringe, 10 µl, readable to 0.1 µl.

Pump

29 A pump, with adjustable flow rate, capable of being worn by people while carrying out their normal work, and capable of running continuously for 8 hr at the recommended flow rate. The pump flow rate should be stable to within ± 5% (±2CV) and the total volume of air sampled by the pump over the recommended sampling period should be within ± 10% (±2CV) of the calculated volume.

Notes

The sampling pump should be in accordance with local safety regulations.

If a diaphragm pump is used, the stroke volume should be calibrated before and after sampling.

Flow rates below 5 ml/min should not be used (see paragraph 42). An effective flow rate below this value can be achieved by intermittent sampling, but diffusive sampling will occur during the 'off' cycles.

Plastic or rubber tubing

30 Plastic or rubber tubing, about 90 cm long, of appropriate diameter to ensure a leak-proof fit to both pump and sample tube or tube holder, if used. Clips should be provided to hold the sample tube and connecting tubing to the wearer's lapel area.

Note

Sampling tubes should not be used with plastic or rubber tubing upstream of the sorbent. Interferences by the tubing may introduce sampling errors.

Soap bubble meter

31 A soap bubble meter or other suitable device for calibrating pump.

Gas chromatograph

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

33 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[7] (paragraph 52).

Injection facility for preparing standards

34 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.

PROCEDURE

Calibration of sampling pump

35 Calibrate the sampling pump with a representative sorbent tube assembly in line, using an appropriate external calibrated meter.

Sampling

36 Select a sorbent tube (or tube combination) appropriate for the compound or mixture to be sampled. Guidance on suitable sorbents is given in Tables 2 to 6. If more than one tube is to be used, prepare a tube assembly by joining the tubes with a union (paragraph 27). Attach the pump to the sorbent tube or tube assembly with plastic or rubber tubing, so that the tube containing the stronger sorbent is nearest the pump.

37 When used for personal sampling, to minimise channelling, the tube assembly should be mounted vertically in the worker's breathing zone, for example on his or her lapel. The pump is attached to the worker as appropriate to minimise inconvenience. When used for fixed location sampling, a suitable sampling site is chosen.

38 Turn the pump on and adjust the flow rate so that the recommended sample volume is taken in the available time. The recommended air sample volume for the volatile organic compounds covered by this method is 2.5 litres and the equivalent 8-hr sampling rate, 5 ml/min. For sampling over shorter periods, the flow rate may be increased in proportion, but should not exceed 200 ml/min. Thus, a 10-min sample may be taken at 200ml/min. If the total sample is likely to exceed 1 mg (ie 1 mg on each tube), the sample volume should be reduced accordingly, or electrometer overload may occur. At higher temperatures than 20°C, the safe sampling volume is reduced by a factor of 2 for each 10°C rise in temperature.

39 Note and record the times, temperature, flow rate or register reading if appropriate and the barometric pressure when the pump was turned on. At the end of the sampling period, note and record the flow rate or register reading, turn the pump off, and note and record the time, temperature and barometric pressure. Disconnect the sample tube assembly and seal both ends of each tube with compression seals. Tighten these seals securely. Place identifying labels on each tube. If samples are not to be analysed within 8 hours, they should be placed in a sealed inert container.

Blanks

40 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.

41 Sampling efficiency will be 100%, 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, while monitoring the effluent air with a flame ionization or equivalent detector. Alternatively, the breakthrough volume may be determined by an indirect, chromatographic, method.[8]

Breakthrough volume

42 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 or above 500 ml/min. Sampling flow rates should thus be set between 5 and 500 ml/min (optimum 50 ml/min). The breakthrough volumes of Spherocarb and of carbon are less affected by temperature and flow rate, but are substantially reduced

at high concentrations of volatile organic vapour or high relative humidity. To allow a suitable margin of safety, it is recommended that sample volumes of not more than 70% of the breakthrough volume or 50% of the retention volume (the breakthrough volume of a single injection of vapour) be taken. Tables 2-6 give typical values for retention volumes and safe sampling volumes.

Influence of humidity

43 The safe sampling volumes in Tables 2-6 have been determined by the chromatographic method[8] which does not take account of humidity. Measurements by the direct method indicate that breakthrough volumes at high (95%) 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 are also anticipated, the breakthrough volumes for carbonaceous sorbents should be further reduced by a factor of two.

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

44 Accurately weigh approximately 1 g of each of the substances in mixture 1 (paragraph 14) 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 (paragraphs 15 and 16) if required.

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

45 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.

46 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

47 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

48 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 34) 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 then 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 44, and 4 µl, 2 µl and 1 µl of solution 45. Also load sorbent tubes with 4 µl of control solution 46.

Desorption and analysis

49 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.

50 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 (the same sorbent as in the sample tube) 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.

51 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

52 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 13 are given in Table 7.

53 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.

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

Calibration

55 Analyse each sorbent tube standard (paragraph 48) 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 44 or 45 x volume injected (µl; paragraph 48).

56 Check the calibration graph by analysing the independently prepared control solution 46 (standard tube 48). 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

57 Analyse the samples and sample blanks as described for the calibration standards in paragraph 55. Determine the peak response and read from the calibration graph the mass of the analyte in the desorbed sample.

Determination of desorption efficiency

58 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 55. This calibration should be the same or nearly the same as that in paragraph 55. 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.

59 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 14). 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 13 are given in Table 7. Response factors for other compounds may be calculated approximately from effective carbon numbers.[9] If the ratio of the slopes of the calibration graphs does 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 48) a second time; the second desorption should give a peak response less than 5% of the first.

60 Ideally, desorption efficiencies should be determined on tube standards loaded from a standard atmosphere (ref 2, MDHS 3 or 4), 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.

CALCULATIONS

Mass concentration of analyte

61 Calculate the concentration of the analyte in the sampled air, in mg/m^3, by means of the following equation:

$$C = \frac{F - B}{V}$$

where:

C is the concentration of analyte in the air sampled, in mg/m^3;

F is the mass of analyte present in the actual sample as found in paragraph 57, in µg (sum of tubes if more than one used);

B is the mass of analyte present in the blank tube, in µg (sum of tubes if more than one used);

V is the volume of sample taken, in litres.

Note

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

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

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

62 Calculate the volume fraction of the analyte in air, in ppm by means of the following equation:

$$C' = C \cdot \frac{24.5}{M} \cdot \frac{101}{P} \cdot \frac{T}{298}$$

where:

C' is the volume fraction of the analyte in air, in ppm;
M is the molecular mass of the analyte of interest, in g/mol.

Total concentration of vapours

63 Calculate the total concentration of vapours, in mg/m^3 or ppm, by summing the individual contributions calculated in paragraphs 61 and 62 respectively.

REPORT

64 The test report should 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 Precision and storage recovery of organic vapours on Tenax tubes (paragraph 11)

Organic compound	*Loading* µg	*time = 0* *%CV**	*time = 5 months* *mean recovery** + %CV**		*time = 11 months* *mean recovery** + %CV**	
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	nd	nd	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	(100.0)	1.8	(100.0)	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
trimethylbenzene	10.2	1.7	101.6	0.5	101.3	0.8
Esters and glycol ethers						
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
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	1.0	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*				
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	20.0	5.5	99.3***	1.9	107.5****	2.4

*6 replicates

** normalised to toluene = 100. The stability of toluene has been established in a BCR intercomparison[10]

***storage for 1 week

****storage for 4 weeks

Table 2 Extrapolated retention volumes and safe sampling volumes for organic vapours sampled on a 200 mg Tenax sorbent tube at 20°C[8]

Organic compound	*Boiling point (°C)*	*Retention volume (litres)*	*Safe sampling volume (SSV) (litres)*	*SSV per gram (litres)*	*Desorption temp. (°C)*
Hydrocarbons					
hexane	69	6.4	3.2	16	110
heptane	98	34	17	85	130
octane	125	160	80	390	140
nonane	151	1400	700	3500	150
decane	174	4200	2100	10k	160
undecane	196	25k	12k	60k	170
dodecane	216	126k	63k	300k	180
benzene	80	12.5	6.2	31	120
toluene	111	76	38	190	140
xylene	138-144	600	300	1500	140
ethylbenzene	137	360	180	900	145
propylbenzene	159	1700	850	4000	160
isopropylbenzene	152	960	480	2400	160
ethyltoluene	162	2000	1000	5000	160
trimethylbenzene	165-176	3600	1800	8900	170
styrene	145	600	300	1500	160
methylstyrene	167	2400	1200	6000	170
Chlorinated hydrocarbons					
carbon tetrachloride	76	12.4	6.2	31	120
1,2-dichloroethane	84	10.8	5.4	27	120
1,1,1-trichloroethane	74	*not recommended on Tenax*			
1,1,2-trichloroethane	114	68	34	170	120
1,1,1,2-tetrachloroethane	130	156	78	390	150
1,1,2,2-tetrachloroethane	146	340	170	850	150
trichloroethylene	87	11.2	5.6	28	120
tetrachloroethylene	121	96	48	240	150
chlorobenzene	131	52	26	130	140
epichlorohydrin	118	26	13	65	130
Esters and glycol ethers					
ethyl acetate	71	7.2	3.6	18	120
propyl acetate	102	36	18	92	140
isopropyl acetate	90	12	6	31	120
butyl acetate	126	170	85	420	150
isobutyl acetate	115	265	130	650	130
t-butyl acetate	98	*not recommended on Tenax*			
methyl acrylate	81	13	6.5	32	120
ethyl acrylate	100	48	24	120	120
methyl methacrylate	100	55	27	130	120
methoxyethanol	125	6	3	15	120
ethoxyethanol	136	10	5	25	130
butoxyethanol	170	70	35	170	140
methoxypropanol	118	27	13	65	115
methoxyethyl acetate	145	16	8	40	120
ethoxyethyl acetate	156	30	15	75	140
butoxyethyl acetate	192	300	150	750	160
Aldehydes and ketones					
methyl ethyl ketone	80	6.4	3.2	16	120
methyl isobutyl ketone	118	52	26	130	140
cyclohexanone	155	340	170	850	150
3,5,5-trimethylcyclohex-2-enone	214	11 200	5600	28 000	190
furfural	162	600	300	1500	200
Alcohols					
butanol	118	10	5	25	120
isobutanol	108	5.6	2.8	14	120
t-butanol	83	*not recommended on Tenax*			
octanol	180	2800	1400	7000	160
phenol	182	480	240	1200	190
Miscellaneous					
maleic anhydride	202	176	88	440	180
pyridine	116	16	8	40	150
aniline	184	440	220	1100	190
nitrobenzene	211	28 000	14 000	70 000	200

Table 3 Extrapolated retention volumes and safe sampling volumes for organic vapours sampled on a 300 mg Chromosorb 106 sorbent tube at 20°C

Organic compound	*Boiling point (°C)*	*Retention volume (litres)*	*Safe sampling volume** (SSV) (litres)*	*SSV** per gram (litres)*	*Desorption temp. (°C)*
Hydrocarbons					
pentane	35	11.2	5.5	18	127
hexane	69	60	30	100	140
heptane	98	325	160	530	180
octane	125	2076	1000	3300	200
nonane	151	14k	7k	23k	220
decane	174	74k	37k	120k	240
benzene	80	53	26	87	160
toluene	111	165	80	270	200
xylene	138-144	1554	770	2600	250
ethylbenzene	136	730	360	1200	250
trimethylbenzene	165-176	5650	2800	9300	250
Chlorinated hydrocarbons					
carbon tetrachloride	76	44	22	73	160
1,2-dichloroethane	84	34	17	67	150
1,1,1-trichloroethane	74	54	27	89	160
epichlorohydrin	118	98	49	250	180
dichloromethane	40	4.2	2.1	7	120
trichloroethylene	86	80	40	140	170
Esters and glycol ethers					
methyl acetate	58	5.2	2.6	8.7	125
ethyl acetate	71	39	20	67	150
propyl acetate	102	297	150	500	170
isopropyl acetate	90	147	75	250	165
butyl acetate	126	1460	730	2400	195
isobutyl acetate	115	880	440	1500	190
t-butyl acetate	98	327	160	530	185
methoxyethanol	125	9.6	5	17	120
ethoxyethanol	136	150	75	200	250
methoxyethyl acetate	145	1720	860	2900	250
ethoxyethyl acetate	156	8100	4000	13k	250
Ketones					
acetone	56	2.9	1.5*	5	120
methyl ethyl ketone	80	21	10	33	145
methyl isobutyl ketone	118	490	250	830	190
Alcohols					
ethanol	78	2.4	1.2*	4	100
n-propanol	97	17	8	27	125
isopropanol	82	9	44	15	120
n-butanol	118	96	50	170	155
isobutanol	108	60	30	100	150

*SSV below recommended 2.5 litres. Porapak N is preferred (Table 4)

**Reduce SSV by factor of 2 if sampling at high humidity (paragraph 43)

Table 4 Extrapolated retention volumes and safe sampling volumes for organic vapours sampled on a 500 mg Porapak N sorbent tube at 20°C[11]

Organic compound	*Boiling point (°C)*	*Retention volume (litres)*	*Safe sampling volume* (SSV) (litres)*	*SSV* per gram (litres)*	*Desorption temp. (°C)*
Hydrocarbons					
pentane	35	8.2	4.1	8.2	180
hexane	69	32	16	32	180
heptane	98	190	95	190	180
benzene	80	52	26	52	180
Alcohols					
ethanol	78	7.5	3.7	7.5	120
propanol	97	40	20	40	120
butanol	118	10	5	25	120
isobutanol	108	5.6	2.8	14	120
octanol	180	2800	1400	7000	160
phenol	182	480	240	1200	190
Miscellaneous					
acetic acid	116	97	50	97	180
acetonitrile	82	7	3.5	7	180
acrylonitrile	77	16	8	16	180
propionitrile	97	23	11	23	180
pyridine	116	390	200	390	180
2-butanone	80	95	50	95	180

*Reduce SSV by factor of 2 if sampling at high humidity (paragraph 43)

Table 5 Extrapolated retention volumes and safe sampling volumes for organic vapours sampled on a 300 mg Spherocarb sorbent tube at 20°C

Organic compound	*Boiling point (°C)*	*Retention volume (litres)*	*Safe sampling volume** (SSV) (litres)*	*SSV ** per gram (litres)*	*Desorption temp. (°C)*
butane	-0.5	1640	820	2700	270
pentane	35	63k	30k	100k	335
hexane	69	3.9M	2M	7M	390
benzene	80	1M	500k	1700k	375
dichloromethane	40	395	200	700	250
1,1,1-trichloroethane	74	17.6k	8k	27k	290
methanol	65	264*	130	430	340
ethanol	78	6900*	3500	12k	370

*Limited data

**Reduce SSV by factor of 10 if sampling at high humidity; reduce SSV by factor of 2 if sampling at high concentration (paragraph 43)

Table 6 Extrapolated retention volumes and safe sampling volumes for organic vapours sampled on a 300 mg charcoal sorbent tube at 20°C

Organic compound	*Boiling point (°C)*	*Retention volume (litres)*	*Safe sampling volume* (SSV) (litres)*	*SSV* per gram (litres)*	*Desorption temp. (°C)*
propane	-42	10**	5	15	220**
butane	-0.5	900**	450	600	270**
pentane	35	27k	13k	43k	327
hexane	69	1.5M	750k	2.5M	388
benzene	80	340k	170k	560k	370

*Reduce SSV by factor of 10 if sampling at high humidity; reduce SSV by factor of 2 if sampling at high concentration (paragraph 43)

**Extrapolated from data on pentane, hexane and benzene

Table 7 Identification of components on BP-1 and BP-10 capillary columns operated as specified in paragraph 52. 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	1.00
isopropylbenzene	919	983	0.97
o-ethyltoluene	975	1047	1.02
m-ethyltoluene	956	1022	1.01
p-ethyltoluene	958	1023	1.00
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	0.60
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	0.50
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

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