

# Indoor, ambient and workplace air — Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography —

## Part 2: Diffusive sampling

The European Standard EN ISO 16017-2:2003 has the status of a  
British Standard

ICS 13.040.01

## National foreword

This British Standard is the official English language version of EN ISO 16017-2:2003. It is identical with ISO 16017-2:2003.

The UK participation in its preparation was entrusted by Technical Committee EH/2, Air quality, to Subcommittee EH/2/3, Ambient atmospheres, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this subcommittee can be obtained on request to its secretary.

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### Summary of pages

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English version

Indoor, ambient and workplace air - Sampling and analysis of  
volatile organic compounds by sorbent tube/thermal  
desorption/capillary gas chromatography - Part 2: Diffusive  
sampling (ISO 16017-2:2003)

Air intérieur, air ambiant et air des lieux de travail -  
Echantillonnage et analyse des composés organiques  
volatils par tube à adsorption/désorption  
thermique/chromatographie en phase gazeuse sur  
capillaire - Partie 2: Echantillonnage par diffusion (ISO  
16017-2:2003)

Innenraumluft, Außenluft und Luft am Arbeitsplatz -  
Probenahme und Analyse flüchtiger organischer  
Verbindungen durch Sorptionsröhrchen/thermische  
Desorption/Kapillar- Gaschromatographie - Teil 2:  
Probenahme mit Passivsammlern (ISO 16017-2:2003)

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This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

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## Foreword

This document (EN ISO 16017-2:2003) has been prepared by Technical Committee ISO/TC 146 "Air quality" in collaboration with Technical Committee CEN/TC 264 "Air quality", the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by November 2003, and conflicting national standards shall be withdrawn at the latest by November 2003.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and the United Kingdom.

## Endorsement notice

The text of ISO 16017-2:2003 has been approved by CEN as EN ISO 16017-2:2003 without any modifications.

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**Indoor, ambient and workplace air —  
Sampling and analysis of volatile organic  
compounds by sorbent tube/thermal  
desorption/capillary gas  
chromatography —**

**Part 2:  
Diffusive sampling**

*Air intérieur, air ambiant et air des lieux de travail — Échantillonnage et  
analyse des composés organiques volatils par tube à  
adsorption/désorption thermique/chromatographie en phase gazeuse  
sur capillaire —*

*Partie 2: Échantillonnage par diffusion*



Reference number  
ISO 16017-2:2003(E)



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## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 16017-2 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 6, *Indoor air*.

ISO 16017 consists of the following parts, under the general title *Indoor, ambient and workplace air — Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography*:

- *Part 1: Pumped sampling*
- *Part 2: Diffusive sampling*



# Indoor, ambient and workplace air — Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography —

## Part 2: Diffusive sampling

### 1 Scope

This part of ISO 16017 gives general guidance for the sampling and analysis of volatile organic compounds (VOCs) in air. It is applicable to indoor, ambient and workplace air.

This part of ISO 16017 is applicable to a wide range of VOCs, including hydrocarbons, halogenated hydrocarbons, esters, glycol ethers, ketones and alcohols. A number of sorbents<sup>1)</sup> are recommended for the sampling of these VOCs, each sorbent having a different range of applicability. Very polar compounds generally require derivatisation; very low boiling compounds are only partially retained by the sorbents and can only be estimated qualitatively. Semi-volatile compounds are fully retained by the sorbents, but may only be partially recovered.

This part of ISO 16017 is applicable to the measurement of airborne vapours of VOCs in a mass concentration range of approximately 0,002 mg/m<sup>3</sup> to 100 mg/m<sup>3</sup> individual organic for an exposure time of 8 h, or 0,3 µg/m<sup>3</sup> to 300 µg/m<sup>3</sup> individual organic for an exposure time of four weeks.

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 or by the sample splitting capability of the analytical instrumentation used. The lower limit of the useful range depends on the noise level of the detector and on blank levels of analyte and/or interfering artefacts on the sorbent tubes. Artefacts are typically sub-nanogram for well-conditioned Tenax GR and carbonaceous sorbents such as Carbopack/Carbotrap type materials, carbonized molecular sieves such as Spherocarb and pure charcoals. Artefacts are typically at low nanogram levels for Tenax TA and at 5 ng to 50 ng levels for other porous polymers such as Chromosorb and Porapak.

### 2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 16000-1, *Indoor air — Part 1: General aspects of sampling strategy*

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1) The sorbents listed in Annex B and elsewhere in this part of ISO 16017 are those known to perform as specified under this part of ISO 16017. Each sorbent or product that is identified by a trademarked name is unique and has a sole manufacturer; however, they are widely available from many different suppliers. This information is given for the convenience of users of this part of ISO 16017 and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

### 3 Principle

The diffusive sampler (or samplers) is exposed to air for a measured time period. The rate of sampling is determined by prior calibration in a standard atmosphere (see 8.6). The organic vapour migrates down the tube by diffusion and is collected on the sorbent (see Annex A). The collected vapour (on each tube) is desorbed by heat and is transferred under inert carrier gas into a gas chromatograph equipped with a capillary column and a flame ionization detector or other suitable detector, where it is analysed. The analysis is calibrated by means of liquid or vapour spiking onto a sorbent tube.

Information on possible saturation of the sorbent bed, the effect of transients and the effect of face velocity is given in Annex A. Annex A also explains the dependence of effective uptake rates on the concentration level of pollutants and the time of diffusive sampling, for non-ideal sorbents, which results in different values being given in Tables 1 and 2. Further detailed information on the theory of performance of diffusive samplers is given in prEN 13528-3 [1].

### 4 Reagents and materials

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

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

#### 4.1 Volatile organic compounds.

A wide range of VOCs are required as reagents for calibration purposes, using either liquid spiking (4.7 and 4.8) or vapour spiking (4.4 to 4.6) onto sorbent tubes.

#### 4.2 Dilution solvent, for preparing calibration blend solutions for liquid spiking (4.7).

The solvent should be of chromatographic quality. It shall be free from compounds co-eluting with the compound(s) of interest (4.1).

NOTE Methanol is frequently used. Alternative dilution solvents, e.g. ethyl acetate or cyclohexane, can be used, particularly if there is no possibility of reaction or chromatographic co-elution.

#### 4.3 Sorbents, preferably of particle size 0,18 mm to 0,25 mm (60 mesh to 80 mesh).

Each sorbent should be preconditioned under a flow of inert gas by heating it overnight at a temperature at least 25 °C below the published maximum for that sorbent before packing the tubes. They shall be kept in a clean atmosphere during cooling to room temperature, storage, and loading into the tubes. Wherever possible, analytical desorption temperatures should be kept below those used for conditioning. Tubes prepaced by the manufacturer are also available for most sorbents and as such only require conditioning. Care should be taken with the disposal of the sorbents, using normal laboratory practice.

NOTE A guide for sorbent selection is given in Annex C. Equivalent sorbents may be used. A guide to sorbent conditioning and analytical desorption parameters is given in Annex D. In most cases the sorbents can be used for indoor air measurements as well as for ambient air and workplace atmosphere measurements.

#### 4.4 Calibration standards.

Calibration standards are preferably prepared by loading required amounts of the compounds of interest on sorbent tubes from standard atmospheres (see 4.5 and 4.6), as this procedure most closely resembles the practical sampling situation.

If this way of preparation is not practicable, standards may be prepared by a liquid spiking procedure (see 4.7 and 4.8) provided that the accuracy of the spiking technique is established by one of the following methods:

- a) by using procedures giving spiking levels fully traceable to primary standards of mass and/or volume;

- b) confirmed by comparison with reference materials, if available;
- c) confirmed by comparison with standards produced using standard atmospheres;
- d) confirmed by comparison with results of reference measurement procedures.

#### 4.5 Standard atmospheres, of known concentrations of the compound(s) of interest.

Prepare standard atmospheres by an independent method. Methods described in ISO 6141 and several parts of ISO 6145 are suitable (see Bibliography). If the procedure is not applied under conditions that allow the establishment of full traceability of the generated concentrations to primary standards of mass and/or volume, or if the chemical inertness of the generation system cannot be guaranteed, the concentrations shall be confirmed using an independent procedure.

#### 4.6 Standard sorbent tubes, loaded by spiking from standard atmospheres.

Prepare loaded sorbent tubes by passing an accurately known volume of the calibration atmosphere through the sorbent tube, e.g. by means of a pump. The volume of atmosphere sampled shall not exceed the breakthrough volume of the analyte-sorbent combination. After loading, disconnect and seal the tube. Prepare fresh standards with each batch of samples. Prepare standard atmospheres of mass concentrations equivalent to 10 mg/m<sup>3</sup> and 100 µg/m<sup>3</sup>. For workplace air, load sorbent tubes with 100 ml, 200 ml, 400 ml, 1 l, 2 l, or 4 l of the 10 mg/m<sup>3</sup> atmosphere. For ambient or indoor air load sorbent tubes with 100 ml, 200 ml, 400 ml, 1 l, 2 l, 4 l or 10 l of the 100 µg/m<sup>3</sup> atmosphere.

#### 4.7 Solutions for liquid spiking.

##### 4.7.1 Solution containing approximately 10 mg/ml of each liquid component.

Accurately weigh approximately 1 g of substance or substances of interest into a 100 ml volumetric flask, starting with the least volatile substance. Make up to 100 ml with dilution solvent (4.2), stopper and shake to mix.

##### 4.7.2 Solutions containing approximately 1 mg/ml of liquid components.

Introduce 50 ml of dilution solvent into a 100 ml volumetric flask. Add 10 ml of solution 4.7.1. Make up to 100 ml with dilution solvent, stopper and shake to mix.

##### 4.7.3 Solution containing approximately 100 µg/ml of each liquid component.

Accurately weigh approximately 10 mg of substance or substances of interest into a 100 ml volumetric flask, starting with the least volatile substance. Make up to 100 ml with dilution solvent (4.2), stopper and shake to mix.

##### 4.7.4 Solution containing approximately 10 µg/ml of liquid components.

Introduce 50 ml of dilution solvent into a 100 ml volumetric flask. Add 10 ml of solution 4.7.3. Make up to 100 ml with dilution solvent, stopper and shake to mix.

##### 4.7.5 Solution containing approximately 1 mg/ml of gas components.

For gases, e.g. ethylene oxide, a high-level calibration solution can be prepared as follows. Obtain gas at atmospheric pressure by filling a small plastic gas bag from a gas cylinder containing pure gas. Fill a 1 ml gas-tight syringe with 1 ml of the pure gas and close the valve of the syringe. Using a 2 ml septum vial, add 2 ml dilution solvent and close with the septum cap. Insert the tip of the syringe needle through the septum cap into the dilution solvent. Open the valve and withdraw the plunger slightly to allow the dilution solvent to enter the syringe. The action of the gas dissolving in the dilution solvent creates a vacuum, and the syringe fills with solvent. Return the solution to the flask. Flush the syringe twice with the solution and return the washings to the flask. Calculate the mass of gas added using the gas laws, i.e. 1 mole of gas at STP (standard temperature and pressure: 273,15 K and 1 013,25 hPa) occupies 22,4 litres.

#### **4.7.6 Solution containing approximately 10 µg/ml of gas components**

For gases, e.g. ethylene oxide, a low level calibration solution may be prepared as follows. Obtain pure gas at atmospheric pressure by filling a small plastic gas bag from a gas cylinder. Fill a 10 µl gas-tight syringe with 10 µl of the pure gas and close the valve of the syringe. Using a 2 ml septum vial, add 2 ml dilution solvent and close with the septum cap. Insert the tip of the syringe needle through the septum cap into the dilution solvent. Open the valve and withdraw the plunger slightly to allow the dilution solvent to enter the syringe. The action of the gas dissolving in the dilution solvent creates a vacuum, and the syringe fills with solvent. Return the solution to the flask. Flush the syringe twice with the solution and return the washings to the flask. Calculate the mass of gas added using the gas laws, i.e. 1 mole of gas at STP occupies 22,4 litres.

#### **4.8 Standard sorbent tubes loaded by liquid spiking**

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 (5.7) through which inert purge gas is passed at 100 ml/min and a 1 µl 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. For workplace air, load sorbent tubes with 1 µl to 5 µl of solution 4.7.1, 4.7.2 or 4.7.5. For ambient and indoor air, load sorbent tubes with 1 µl to 5 µl of solution 4.7.3, 4.7.4 or 4.7.6.

## **5 Apparatus**

Use ordinary laboratory apparatus and the following devices.

### **5.1 Sorbent tubes.**

These tubes shall be compatible with the thermal desorption apparatus to be used (5.6). Typically, but not exclusively, they are constructed of stainless steel tubing of dimensions 6,3 mm (1/4 in) OD, 5 mm ID and 90 mm long. Tubes of other dimensions may be used, but the uptake rates given in Table 1 are based on these tube dimensions. For labile analytes, such as sulfur-containing compounds, glass-lined or glass tubes (typically 4 mm ID) should be used. Mark one end of the tube, for example by a scored ring, about 10 mm from the (diffusive) sampling end. Pack the tubes with preconditioned sorbents so that the sorbent bed will be within the desorber heated zone and a consistent gap of about 14 mm is retained at the marked (diffusive) end of the tube.

Uptake rates in Table 1 are given for tubes with a nominal air gap (between sorbent bed and diffusive end cap) of at least 14 mm. In practice, packed tube dimensions vary<sup>[2]</sup>, and tubes should be rejected where the air gap (between stainless steel screen retaining the sorbent bed and the end of the tube) is outside the range 14,0 mm to 14,6 mm.

Tubes contain between 200 mg and 1 000 mg sorbent, depending on sorbent density, which is typically about 250 mg porous polymer, or 500 mg carbon molecular sieve or graphitized carbon. The sorbents are retained by a stainless steel gauze at the diffusion end and an unsilanized glass wool plug and/or a second stainless gauze at the other end.

### **5.2 Sorbent tube end caps.**

The tubes shall be sealed, e.g. with metal screw cap fittings with PTFE seals.

### **5.3 Sorbent tube end caps for sampling.**

The diffusive end cap is similar to 5.2, but allows 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 end cap incorporate a silicone membrane next to the gauze.

#### 5.4 Syringes.

A precision 10 µl liquid syringe readable to 0,1 µl, a precision 10 µl gas-tight syringe readable to 0,1 µl and a precision 1 ml gas-tight syringe readable to 0,01 ml.

**5.5 Gas chromatograph**, fitted with a flame ionization detector, photoionization detector, mass spectrometric or other suitable detector capable of detecting an injection of 0,5 ng toluene with a signal-to-noise ratio of at least 5 to 1, and including a gas chromatograph capillary column capable of separating the analytes of interest from other components.

**5.6 Thermal desorption 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.

A typical apparatus contains a mechanism for holding the tubes to be desorbed whilst they are heated and purged simultaneously with inert carrier gas. The desorption temperature and time is adjustable, as is the carrier gas flow rate. The apparatus should also incorporate additional features, such as automatic sample tube loading, leak-testing, and a cold trap in the transfer line to concentrate the desorbed sample (8.2). The desorbed sample, contained in the purge gas, is routed to the gas chromatograph and capillary column via a heated transfer line.

#### 5.7 Injection facility for preparing standards by liquid spiking.

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 an O-ring seal.

### 6 Sample tube conditioning

Prior to use, tubes should be reconditioned by desorbing them at a temperature at or just above the analytical desorption temperature (see Annex D) for 10 min with a carrier gas flow of at least 100 ml/min. The carrier gas flow should be towards the diffusive sampling end to prevent recontamination of the sorbents. Tubes should then be analysed, using routine analytical parameters, to ensure that the thermal desorption blank is sufficiently small. If the blank is unacceptable, tubes should be reconditioned by repeating this procedure. Once a sample has been analysed, the tube may be reused to collect 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 with metal screwcaps with combined PTFE ferrule fittings and stored in an airtight container when not sampling or being conditioned.

NOTE The sorbent tube blank level is acceptable if interfering peaks are no greater than 10 % of the typical areas of the analytes of interest.

### 7 Sampling

Select a sorbent tube (or tubes) appropriate for the compound or mixture to be sampled. Guidance on suitable sorbents is given in Tables 1 and 2 and Annex B.

Immediately before sampling, remove the storage 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.

When used for personal sampling, the tube(s) should be mounted in the breathing zone. When used for fixed-location sampling, choose a suitable site; for indoor air in accordance with ISO 16000-1. For ambient air, recommendations for site selection and for the protection of samples from adverse environmental conditions are given in Annex A and prEN 13528-3 [1]. Attention shall be paid to three main considerations: air velocity, protection from precipitation, and security. More information is given in the next paragraph, in A.5 and reference [1].

Expose the sampling tubes only under conditions where the face velocity requirement can be expected to be satisfied. For the tubes specified in 5.1 with end caps 5.3, wind speed (air velocity) has no influence. Other devices may have different requirements, including also a minimum wind speed.

Instruments to measure wind speeds as low as 0,007 m/s are not commonly available, so the wind speed may have to be measured indirectly. The user is also cautioned about the possible influence of very high wind speeds (above 12 m/s) for which performance characteristics are currently unavailable.

The recommended exposure time for the VOCs covered by this part of ISO 16017 is 8 h for workplace monitoring and four weeks for ambient and indoor air monitoring. Sampling over shorter periods is possible, down to 30 minutes for workplace monitoring and one week for ambient and indoor air monitoring, but the monitored concentration range will be changed accordingly. For example, for a 4-h sampling period, the working range is approximately 0,004 mg/m<sup>3</sup> to 200 mg/m<sup>3</sup>.

NOTE The working ranges specified in the Scope (see Clause 1) for 8 h and 4 weeks are not equivalent because they depend on the choice of sorbent, different diffusive uptake rates and different practical applications.

Note and record the times, temperature and the barometric pressure at the start of the sampling period. At the end of the sampling period, again note and record the time, temperature and barometric pressure.

Replace the diffusion end cap with a storage end cap and tighten the seal securely. The tubes should be uniquely labeled. Solvent containing paints and markers or adhesive labels should not be used to label the tubes.

If samples are not to be analysed within 8 h, place them in a clean, uncoated, sealed metal or glass container.

Record air temperature and barometric pressure periodically during sampling, if it is desired to express concentrations reduced to specific conditions (9.1).

Field 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. For the field blanks end caps are used instead of diffusion caps. Label these as blanks.

## 8 Procedure

### 8.1 Safety precautions

This part of ISO 16017 does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this part of ISO 16017 to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

### 8.2 Desorption and analysis

#### 8.2.1 Desorption

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 stationary phase. 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 shall be towards the diffusive sampling end, i.e. the marked end of the tube should be nearest the gas chromatograph column inlet. The gas flowrate through the tube should be on the order of 30 ml/min to 50 ml/min for optimum desorption efficiency. During the purge period, care should be taken to minimize heating of the tube.

NOTE 1 For the initial air purge, it is usually necessary to use 10 × the tube volume (i.e. 20 ml to 30 ml) of inert gas to completely displace the volume of air (2 ml to 3 ml) in the tube. However, if strongly hydrophilic sorbents are needed, it may be necessary to employ a larger purge to reduce sorbed air and water to prevent ice formation blocking the cold trap.

The desorbed sample occupies a volume of several millilitres of gas, so that pre-concentration is essential prior to capillary GC analysis. This may be achieved using a small, cooled, secondary sorbent trap, which can be desorbed sufficiently rapidly at low flowrates (< 5 ml/min) to minimize band broadening, and produce capillary-compatible peaks. Alternatively, an empty secondary trap, or one containing an inert material such as glass beads, may be used to preconcentrate the sample, but such traps typically require cooling to below – 100 °C. Alternatively, the desorbed sample can be passed directly to the gas chromatograph (single-stage desorption) where it shall be refocused. This typically requires a high phase ratio column (e.g. 5 µm film thickness, 0,2 mm to 0,32 mm ID) and a sub-ambient starting temperature.

If a secondary sorbent cold trap is not available and if sub-zero capillary cryofocusing temperatures are used to preconcentrate the analytes, water should be completely eliminated from the sample tube prior to desorption in order to prevent ice formation which can block the capillary tubing and stop the thermal desorption process.

NOTE 2 If a secondary cold trap is not available and optimum sample tube desorption flowrates of 30 ml/min to 50 ml/min are used, a minimum split ratio of 30:1 to 50:1 is typically required for operation with high-resolution capillary columns. Single-stage thermal desorption may thus limit sensitivity.

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:

Desorption temp	250 °C to 325 °C
Desorption time	5 min to 15 min
Desorption flow rate	30 ml/min to 50 ml/min
Cold trap low	+ 20 °C to – 180 °C, depending on type of cold trap
Cold trap high	250 °C to 350 °C
Cold trap sorbent	typically same as tubes, 40 mg to 100 mg, if used
Carrier gas	helium
Split ratios	Split ratios between the sample tube and secondary trap and between the secondary trap and analytical column (if applicable) should be selected dependent on expected atmospheric concentration. (See guidance from respective manufacturers of the thermal desorption apparatus.)

NOTE 3 The desorption temperature depends on the analyte and the sorbent used. Recommendations for maximum desorption temperatures for particular sorbents are given in Annexes A and C. Due to their potential thermal instability, secondary and tertiary volatile amines and some polyhalogenated compounds having one or two carbon atoms specially brominated compounds may suffer some thermal degradation.

### 8.2.2 Analysis

Set the sample flowpath temperature (transfer line temperature) high enough to prevent analyte condensation but not so high as to cause degradation. Analytes sufficiently volatile to be present in the vapour phase in air at ambient temperature do not usually require flowpath temperatures above 150 °C. However, some types of apparatus may require higher temperatures.

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 depends largely on which compounds, if any, are present that might interfere in the chromatographic analysis. Typical examples are 50 m × 0,22 mm fused silica columns with thick-film (1 µm to 5 µm) dimethylsiloxane or a 50 m 7 % cyanopropyl, 7 % phenyl, 86 % methyl siloxane stationary phase. Typical operating conditions for these columns are a temperature programme from 50 °C to 250 °C at 5 °C/min, with an initial hold time of 10 min at 50 °C.

The capillary column, or preferably a length of uncoated, deactivated fused silica, should be threaded back through the transfer line from the thermal desorption apparatus to the gas chromatograph such that it reaches as close as possible to the sorbent in the cold trap, or as close as possible to the tube in a single-stage desorber. Internal tubing shall be inert and dead volumes shall be minimized. A split valve(s) is conveniently placed at the inlet and/or outlet of the secondary trap. The split valve on the outlet of the secondary trap may be located either at the inlet or the outlet of the transfer line. Split ratios depend on the application.

NOTE Lower split ratios are suitable for ambient (typically 1:1 to 10:1) and indoor air measurements (typically 1:1 to 20:1); higher split ratios for workplace air measurements (typically 100:1 to 1000:1).

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

### 8.3 Calibration

Analyse each sorbent tube standard (4.6 or 4.8) by thermal desorption and gas chromatography.

Prepare a calibration graph by plotting the base-ten logarithm of the areas of the analyte peaks corrected for blank levels on the vertical scale against the base-ten logarithm of the mass of the analyte, in micrograms, on the sorbent tube standard corresponding to the solutions in 4.7 or atmospheres in 4.5.

### 8.4 Determination of sample concentration

Analyse the samples and sample blanks as described for the calibration standards in 8.3. Determine the peak area and read from the calibration graph the mass of the analyte in the desorbed sample [3].

### 8.5 Determination of desorption efficiency

The efficiency of desorption should be checked by comparing the chromatographic response of a sorbent tube standard (8.3) with that obtained by injecting aliquots of the standard solutions or the atmosphere directly into the gas chromatograph. Thus, prepare a second calibration graph of peak area against mass of analyte as in 8.3, but using solutions 4.7 or atmosphere 4.6. This calibration should be the same, or nearly the same, as that in 8.3. 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.

Some makes of thermal desorber do not have a direct liquid injection facility. In these cases, and when loaded tubes are prepared from a calibration blend atmosphere, desorption efficiency should be checked by comparing the calibration graph of the substance of interest (4.1) with that of n-hexane. The ratio of the slope of the calibration graph of the substance of interest relative to that of n-hexane should be the same as the relative response factor for that compound. Response factors for other compounds may be calculated approximately from effective carbon numbers<sup>[1]</sup>. 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.

### 8.6 Calibration of uptake rate

The uptake rates given in Tables 1 and 2 are for tubes with the dimensions given in 5.1 without a membrane in the diffusion end cap (5.3). For other specifications, it may be necessary to follow EN 838<sup>[4]</sup> or EN 13528-2<sup>[5]</sup> to determine the uptake rate.

NOTE Diffusive uptake rate is sometimes dependent on the choice of sorbent (see prEN 13528-3<sup>[1]</sup>).



## 9 Calculations

### 9.1 Mass concentration of analyte

Calculate the mass concentration of the analyte in the sampled air, in micrograms per cubic metre ( $\mu\text{g}/\text{m}^3$ ), by means of Equation (1):

$$\rho = \frac{m_a - m_b}{q_V \cdot t} \times 10^6 \quad (1)$$

where

$\rho$  is the mass concentration of analyte in the air sampled, in micrograms per cubic metre;

$m_a$  is the mass of analyte present in the actual sample as found in 8.4, in micrograms;

$m_b$  is the mass of analyte present in the blank tube, in micrograms;

$q_V$  is the diffusive uptake rate, in cubic centimetres per minute (Table 1 or 8.6);

$t$  is the exposure time, in minutes.

NOTE 1 If  $m_a$  and  $m_b$  are expressed in milligrams, the resultant mass concentration  $\rho$  will be in milligrams per cubic metre.

NOTE 2 If it is desired to express mass concentrations reduced to specified conditions, e.g. 25 °C and 101 kPa, then:

$$\rho_c = \rho \cdot \frac{101}{p} \cdot \frac{T + 273}{298} \quad (2)$$

where

$\rho_c$  is the mass concentration of the analyte in air sampled, reduced to specified conditions, in micrograms per cubic metre;

$p$  is the actual pressure of the air sampled, in kilopascals;

$T$  is the actual temperature of the air sampled, in degrees Celsius.

### 9.2 Volume fraction of analyte

Alternatively, calculate the content (volume fraction) of the analyte in air, in microlitres per cubic metre, by means of the following equation:

$$\varphi = \frac{m_a - m_b}{q_V \cdot t} \times 10^6 \quad (3)$$

where

$\varphi$  is the volume fraction of the analyte in air, in microlitres per cubic metre;

$q_V$  is the diffusive uptake rate in  $\text{ng} \cdot (\mu\text{l})^{-1} \cdot \text{min}^{-1}$  (Table 1 or 8.5)<sup>2)</sup>;

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2)  $\mu\text{l/l}$  is often expressed in the non-ISO units ppm ( $= 10^{-6}$ ).

$t$  is the exposure time, in minutes.

NOTE If  $m_a$  and  $m_b$  are expressed in milligrams, the resultant volume fraction  $\varphi$  will be in ml/m<sup>3</sup>.

### 9.3 Uptake rates

Uptake rates in cm<sup>3</sup>/min and ng (μl/l)<sup>-1</sup> min<sup>-1</sup> are related by Equation (4):

$$q_{V'} = \frac{q_V \cdot M \cdot 293 \cdot p}{24,0 \cdot T \cdot 101} \quad (4)$$

where

$M$  is the molar mass of the analyte of interest, in grams per mole;

24,0 is the molar volume at 20 °C and 101 kPa.

## 10 Interferences

Organic components which have the same, or nearly the same, retention time as the analyte of interest will interfere during the gas chromatographic analysis. Interferences can be minimized by proper selection of gas chromatographic columns and conditions, and by stringent conditioning of both the sorbent tubes and analytical system before use.

The method is suitable for use in atmospheres of up to 95 % relative humidity (RH) for all hydrophobic sorbents such as porous polymers and Carbopack/Carbotrap.

When less hydrophobic, strong sorbents such as pure charcoals or carbonized molecular sieves are used in atmospheres with humidity in excess of 65 % RH, care shall be taken to prevent water interfering with the analytical process.

NOTE Suitable water elimination or reduction procedures include sample splitting, "dry purging" of moisture from the secondary focusing trap, use of a diffusion end cap (5.3) with silicone membrane and reducing the time of sampling.

A sorption tube that initially showed a good level of blank values may give rise to formation of artefacts later. Ozone<sup>[6]</sup> and nitrogen oxides in the presence of water<sup>[7]</sup> may damage Tenax TA. Benzaldehyde and acetophenone are possible products of these reactions.

Since ozone and nitrogen oxides may react with the components to be measured, this shall be considered by choosing sampling volumes as small as possible if gases of this kind are to be expected in larger amounts in the air sampled. If Tenax TA does not show the necessary stability because of the presence of aggressive gases, Carbopack may be used as a sorbent<sup>[8], [9], [10]</sup>.

For environmental applications (Table 2), the procedure has been tested mainly for stable compounds. Artefact formation or degradation of collected susceptible VOCs can occur, particularly in very warm weather and at high ozone concentrations<sup>[4]</sup>. In such circumstances, the user is cautioned to perform collected sampling with an alternative procedure not so affected, e.g. a pumped sorbent tube with an oxidant pre-trap, to demonstrate suitability.

## 11 Performance characteristics

Examples of the performance characteristics, including overall uncertainty, precision, storage and blank levels obtained when testing the procedure described in this part of ISO 16017 are given in Annex D and Tables 3 to 8.

## 12 Test report

The test report shall contain at least the following information:

- a) complete identification of the sample;
- b) reference to this part of ISO 16017 or any supplementary standard;
- c) the sampling location, sampling time period;
- d) the barometric pressure and temperature if required in Clause 9;
- e) the test result;
- f) any unusual features noted during the determination;
- g) any operation not included in this part of ISO 16017, or in the International Standard to which reference is made, or regarded as optional.

## 13 Quality control

An appropriate level of quality control should be employed (reference [18] or equivalent).

The field tube blank is acceptable if artefact peaks are no greater than 10 % of the typical areas of the analytes of interest.

The uptake rates given in Tables 1 and 2 are expected to remain constant during the lifetime of the sample tubes. However, the tubes can become unpacked due to excessive vibration or the sorbent can eventually deteriorate. Tubes should therefore be visually examined frequently, and repacked with fresh sorbent after approximately 100 uses or 2 years, whichever comes first.

Table 1 — Diffusive uptake rates on sorbent tubes (without membrane) as specified in 5.1 — Workplace air application

Compound	Sorbent	Level <sup>a</sup>	Uptake rate <sup>b</sup>	
			cm <sup>3</sup> /min	ng (μl/l) <sup>-1</sup> min <sup>-1</sup>
<b>Hydrocarbons</b>				
1,3-Butadiene	Molecular Sieve 13X	A	0,59	1,30
<i>n</i> -Pentane	Chromosorb 106	A	0,50	1,46
	Carbopack B <sup>c</sup>	B	0,60	1,77
<i>n</i> -Hexane	Chromosorb 106	A	0,50	1,77
Benzene	Tenax TA <sup>d</sup>	A	0,41	1,3
	Porapak Q	A	0,42	1,37
	Tenax GR	B	0,57	1,81
	Chromosorb 106 <sup>e</sup>	B	0,54	1,72
<i>n</i> -Heptane	Chromosorb 106	A	0,48	1,95
	Tenax TA <sup>e</sup>	A	0,43	1,77
	Carbotrap B	B	0,47	1,94
Toluene	Tenax TA <sup>e</sup>	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
<i>n</i> -Octane	Chromosorb 106	A	0,46	2,13
	Tenax TA <sup>e</sup>	A	0,43	2,00
Xylene	Tenax TA <sup>e</sup>	B	0,42	1,82
	Chromosorb 106	B	0,48	2,10
	Tenax GR	B	0,57	2,48
Ethylbenzene	Tenax TA <sup>e</sup>	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 <sup>e</sup>	A	0,47	2,0
	Chromosorb 106	B	0,51	2,15
<i>n</i> -Nonane	Chromosorb 106	A	0,46	2,40
	Tenax TA <sup>e</sup>	A	0,40	2,12
Isopropylbenzene	Chromosorb 106	C	0,46	2,26
	Tenax TA <sup>e</sup>	C	0,46	2,26
	Porapak Q	D	0,51	2,5
Trimethylbenzene	Chromosorb 106	C	0,48	2,37
	Tenax TA <sup>e</sup>	C	0,48	2,37
<i>n</i> -Decane	Tenax TA	A	0,40	2,3

Table 1 (continued)

Compound	Sorbent	Level <sup>a</sup>	Uptake rate <sup>b</sup>	
			cm <sup>3</sup> /min	ng (μl/l) <sup>-1</sup> min <sup>-1</sup>
<b>Halogenated hydrocarbons</b>				
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
Epichlorohydrin	Chromosorb 106	E	0,65	2,45
Perfluorodimethylcyclobutane <sup>d</sup>	Carbotrap	B	0,25	
Perfluoromethylcyclopentane <sup>d</sup>	Carbotrap	B	0,25	
Perfluoromethylcyclohexane <sup>d</sup>	Carbotrap	B	0,25	
<b>Esters and glycol ethers</b>				
Ethyl acetate	Chromosorb 106 <sup>e</sup>	B	0,49	2,00
	Tenax TA	B	0,40	1,60
<i>n</i> -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

Table 1 (continued)

Compound	Sorbent	Level <sup>a</sup>	Uptake rate <sup>b</sup>	
			cm <sup>3</sup> /min	ng (μl/l) <sup>-1</sup> min <sup>-1</sup>
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
2-Methoxypropanol	Chromosorb 106 <sup>e</sup>	B	0,45	1,85
	Tenax TA	B	0,37	1,52
2-Butoxyethyl acetate	Tenax	A	0,38	2,8
<b>Aldehydes and ketones</b>				
Methyl isobutyl ketone (2-methyl-4-pentanone)	Tenax TA	B	0,42	1,71
	Chromosorb 106 <sup>e</sup>	B	0,49	2,01
Cyclohexanone	Tenax TA	D	0,57	2,3
Furfural	Tenax TA	A	0,63	2,5
<b>Alcohols</b>				
Propan-2-ol (isopropanol)	Spherocarb	C	0,81	2,0
<b>Miscellaneous</b>				
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
<p><sup>a</sup> Level A = validation equivalent to EN 838 [4] level 1A  Level B = partial validation equivalent to EN 482 [13]  Level C = calculated: ideal value  Level D = calculated from dynamic breakthrough volume  Level E = calculated from sorption isotherm</p> <p><sup>b</sup> Unless specified, values are for 4 h to 8 h exposures for workplace applications.</p> <p><sup>c</sup> An example of sorbent type not recommended because of varying uptake rate.</p> <p><sup>d</sup> Use nickel gauze instead of stainless steel gauze.</p> <p><sup>e</sup> Preferred sorbent type.</p>				

**Table 2 — Diffusive uptake rates on sorbent tubes (without membrane) as specified in 5.1 — Ambient and indoor air applications**

Component	Sorbent	Exposure time	Uptake rate	Uptake rate	Number of independent estimates	Remarks	Bibliogr. ref.
			(standard deviation)	(standard deviation)			
			cm <sup>3</sup> /min	ng (μl/l) <sup>-1</sup> min <sup>-1</sup>			
Benzene	Tenax TA	1 week	0,46	1,45	1	lab comparison	19
Benzene	Tenax TA	2 weeks	0,32 (0,01)	1,03 (0,04)	2	1 lab/ 1 field comparison	19, 20
Benzene	Tenax TA	4 weeks	0,22 (0,03)	0,70 (0,09)	3	2 lab/ 1 field comparisons	19, 20, 21
Benzene	Carbograph TD-1 or Carbopack B	1 week	0,67 (0,06)	2,14 (0,21)	2	1 lab/ 1 field comparison	11, 22
Benzene	Carbograph TD-1 or Carbopack B	2 weeks	0,63 (0,07)	2,02 (0,22)	4	1 lab/ 3 field comparisons	11, 20, 22
Benzene	Carbograph TD-1 or Carbopack B	4 weeks	0,58 (0,05)	1,85 (0,15)	4	1 lab/ 3 field comparisons	11, 20, 22
Benzene	Chromosorb 106	1 week	0,48 (0,03)	1,52 (0,08)	2	1 lab/ 1 field comparison	11, 22
Benzene	Chromosorb 106	2 weeks	0,47 (0,06)	1,47 (0,22)	5	1 lab/ 4 field comparisons	11, 20, 22, 23, 24
Benzene	Chromosorb 106	4 weeks	0,40 (0,08)	1,28 (0,25)	4	1 lab/ 3 field comparisons	11, 20, 22, 24
Benzene	Ambersorb XAD-4	1 week	0,38	1,21	1	1 lab comparison	26
Toluene	Tenax TA	2 weeks	0,32	1,22	1	1 field comparison	20
Toluene	Tenax TA	4 weeks	0,27 (0,07)	1,03 (0,26)	2	1 lab/ 1 field comparisons	20, 21
Toluene	Carbograph TD-1 or Carbopack B	1 week	0,57 (0,15)	2,16 (0,58)	2	1 lab/ 1 field comparison	11, 22
Toluene	Carbograph TD-1 or Carbopack B	2 weeks	0,56 (0,06)	2,13 (0,24)	4	1 lab/ 3 field comparisons	11, 20, 22
Toluene	Carbograph TD-1 or Carbopack B	4 weeks	0,55 (0,07)	2,07 (0,26)	4	1 lab/ 3 field comparisons	20, 11, 22
Toluene	Chromosorb 106	1 week	0,54 (0,15)	2,05 (0,57)	2	1 lab/ 1 field comparison	11, 22
Toluene	Chromosorb 106	2 weeks	0,51 (0,05)	1,91 (0,18)	5	1 lab/ 4 field comparisons	20, 11, 22, 23, 24
Toluene	Chromosorb 106	4 weeks	0,48 (0,06)	1,82 (0,24)	4	1 lab/ 3 field comparisons	20, 11, 22, 24
Toluene	Ambersorb XAD-4	1 week	0,43	1,62	1	1 lab comparison	26
Xylene	Tenax TA	2 weeks	0,34	1,49	2	1 lab/ 1 field comparison	19, 20

Table 2 (continued)

Component	Sorbent	Exposure time	Uptake rate (standard deviation) cm <sup>3</sup> /min	Uptake rate (standard deviation) ng (μl/l) <sup>-1</sup> min <sup>-1</sup>	Number of independent estimates	Remarks	Bibliogr. ref.
Xylene	Tenax TA	4 weeks	0,33 (0,15)	1,46 (0,67)	3	2 lab/ 1 field comparisons	19, 20, 21
Xylene	Carbograph TD-1 or Carbopack B	1 week	0,54 (0,06)	2,37 (0,29)	2	1 lab/ 1 field comparison	11, 22
Xylene	Carbograph TD-1 or Carbopack B	2 weeks	0,47 (0,04)	2,07 (0,21)	4	1 lab/ 3 field comparisons	20, 11, 22
Xylene	Carbograph TD-1 or Carbopack B	4 weeks	0,44 (0,07)	1,94 (0,29)	4	1 lab/ 3 field comparisons	20, 11, 22
Xylene	Chromosorb 106	1 week	0,55 (0,07)	2,42 (0,30)	2	1 lab/ 1 field comparison	11, 22
Xylene	Chromosorb 106	2 weeks	0,47 (0,07)	2,09 (0,29)	5	1 lab/ 4 field comparisons	20, 11, 22, 23, 24
Xylene	Chromosorb 106	4 weeks	0,43 (0,08)	1,91 (0,35)	4	1 lab/ 3 field comparisons	20, 11, 22, 24
Ethylbenzene	Chromosorb 106	2 weeks	0,53 (0,02)	2,31 (0,07)	2	2 field comparisons	23, 24
Ethylbenzene	Chromosorb 106	4 weeks	0,52	2,24	1	1 field comparison	24
Ethylbenzene	Carbopack B	2 weeks	0,50	2,19	1	1 field comparison	26
Ethylbenzene	Carbopack B	4 weeks	0,52	2,30	1	1 field comparison	26
Trimethylbenzene	Tenax TA	4 weeks	0,54	2,67	1	1 lab comparison	21
Trimethylbenzene	Carbopack B	2 weeks	0,44	2,20	1	1 field comparison	26
Trimethylbenzene	Carbopack B	4 weeks	0,47	2,30	1	1 field comparison	26
Decane	Tenax TA	4 weeks	0,51	2,93	1	1 lab comparison	21
Undecane	Tenax TA	4 weeks	0,53	3,34	1	1 lab comparison	21

In most cases, ambient uptake rates have been determined at mass concentrations typical of urban background levels, i.e. a few micrograms of benzene, toluene or xylene per cubic metre. Rates have been determined either in the laboratory, with test atmospheres themselves checked with an independent method (usually a pumped sorbent tube), or directly against one or more samplers of an independent method under field conditions. Reference [19] gives uptake rates for indoor air, where the concentration levels of the generated test atmosphere were typical of indoor air, i.e. approx. 1 mg/m<sup>3</sup> benzene and approx. 2 mg/m<sup>3</sup> total VOC.

As explained in Annex A, the diffusive uptake rates for workplace, indoor and ambient air may not be the same, because of a dependence of the uptake rate on time of exposure and concentration. The effect is more marked for non-ideal sorbents, e.g. Tenax TA.



Table 3 — Recovery (%) of benzene, toluene and xylene from spiked tubes

Study No.		Recovery results					
		Chromosorb 106			Carbograph TD-1		
		Benzene	Toluene	Xylene	Benzene	Toluene	Xylene
1) UK survey	Mean recovery, %	82,7	87,5	95,9	95,1	100,1	100,6
	± standard deviation	8,3	6,7	10,4	12,1	4,4	10,0
	<i>n</i>	20	19	19	19	20	20
2) VOC air comparison	Mean recovery, %	93,1	99,1	100,5	98,7	100,3	98,5
	± standard deviation	11,9	7,9	5,0	3,0	2,7	2,0
	<i>n</i>	13	13	13	13	13	13
3) World survey	Mean recovery, %	104,8	105,9	98,7	103,7	100,7	100,1
	± standard deviation	11,3	10,1	7,8	4,6	3,2	2,3
	<i>n</i>	16	16	16	16	16	16
Combined 1) to 3)	Mean of means, %	93,5	97,5	98,3	99,2	100,4	99,7
	± standard deviation	11,1	9,3	2,3	4,3	0,3	1,1
	<i>n</i>	3	3	3	3	3	3

In Study 1), the spiked amounts of each hydrocarbon were approximately 80 ng; in Studies 2 and 3, the amounts were approximately 200 ng.

Field blanks (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.

Table 4 — Comparison with the UK VOC air network

Location	VOC results comparison $\mu\text{g}/\text{m}^3$					
	Benzene		Toluene		Xylene	
	Diffusive	VOC air	Diffusive	VOC air	Diffusive	VOC air
Leeds	2,27 ± 0,07	3,33	5,30 ± 0,01	6,75	3,44 ± 0,07	3,99
Belfast	2,10 ± 0,36	2,94	4,44 ± 0,15	6,82	3,34 ± 0,14	3,55
Bristol	2,90 ± 0,33	6,11 <sup>a</sup>	6,45 ± 0,86	2,25 <sup>a</sup>	4,70 ± 0,26	2,70
Cardiff	3,70 ± 0,46	9,5	7,90 ± 0,12	8,38	5,67 ± 0,10	5,15
Eltham	2,55 ± 0,35	4,65	5,92 ± 0,69	10,36	3,55 ± 0,30	3,10
Liverpool	2,12 ± 0,16	1,23	4,55 ± 0,19	0,93	3,86 ± 0,19	0,84
Middlesborough	2,35 ± 0,27	2,93	4,23 ± 0,22	4,59	2,66 ± 0,14	No data
Southampton	3,87 ± 0,73	1,90	8,12 ± 0,68	11,14	5,50 ± 0,20	5,49
UCL (London)	4,06 ± 0,14	6,05	9,67 ± 0,16	10,87	6,79 ± 0,27	7,79
Edinburgh	1,29 ± 0,20	1,81	3,29 ± 0,42	3,78	2,00 ± 0,27	1,89
Harwell	0,66 ± 0,03	0,90	1,46 ± 0,31	0,98	0,60 ± 0,04	No data
Birmingham	1,87 ± 0,27	2,54	4,76 ± 0,31	6,75	4,46 ± 0,27	5,59

The VOC air data should be taken as indicative only, due to low data coverage during the corresponding diffusive sampling period.

<sup>a</sup> Possible transposition of benzene/toluene values in Internet archive.

Table 5 — Pilot world survey — Mean ambient air concentration by diffusive sampling for both sorbents combined

Location	Mass concentration $\mu\text{g}/\text{m}^3 \pm$ standard deviation					<i>n</i>
	Benzene		Toluene		Xylene	
Sweden	1,95 ± 0,08	5,63 ± 0,77	3,49 ± 0,29	4		
Denmark	0,99 ± 0,04	1,44 ± 0,03	0,80 ± 0,07	4 <sup>a</sup>		
USA	0,43 ± 0,07	0,76 ± 0,09	0,47 ± 0,09	4		
Australia	1,94 ± 0,2	5,23 ± 0,69	3,87 ± 0,28	4		
Hungary	2,65 ± 0,09	4,7 ± 0,19	3,27 ± 0,18	4		
Germany	1,75 ± 0,15	5,85 ± 0,56	3,74 ± 0,33	4		
China	12,3 ± 1,08	23,04 ± 2,32	11,64 ± 0,51	4		
Finland	0,84 ± 0,16	2,16 ± 0,6	1,58 ± 0,03	4		
Netherlands	1,55 ± 0,14	3,51 ± 0,27	2,28 ± 0,14	4		
Israel	1,42 ± 0,17	3,24 ± 0,1	2,79 ± 0,08	4		
Mexico	3,05 ± 0,51	23,43 ± 1,28	8,79 ± 0,25	4		
Italy	1,59 ± 0,15	5,39 ± 0,11	3,36 ± 0,41	4		
Brazil	0,42 ± 0,33	2,00 ± 0,59	1,81 ± 0,15	4 <sup>b</sup>		
France	1,81 ± 0,25	7,32 ± 0,31	3,87 ± 0,13	4		
N. Ireland	2,10 ± 0,36	4,44 ± 0,15	3,34 ± 0,14	4		
England	1,37 ± 0,25	4,24 ± 0,09	3,36 ± 0,11	4		

<sup>a</sup> *n* = 3 for toluene and xylene.

<sup>b</sup> *n* = 3 for toluene.

**Table 6 — Precision of analysis and storage** (sealed tubes stored at 25 °C for 2 weeks)  
**of test compounds on Chromosorb 106 and Carboxen 569** <sup>[15]</sup>, (load level 1 µg)

Organic compound	Precision of analysis CV %		Storage recovery %	
	Chromosorb	Carboxen	Chromosorb	Carboxen
Propane		1,8		115
Pentane	1,7		112	
Hexane	2,1; 3,6		104	
Benzene	2,9		100	
Dichloromethane	1,9		114	
1,1,1-Trichloroethane	2,4		101	
Methanol		1,7		64
Ethanol	5,9		96	
Butanol	1,3		101	
Methyl acetate	1,8		113	
Methoxyethanol	5,7		121	
Methyl ethyl ketone	2,2		103	
Acetonitrile	4,1		112	
Butyl acetate	3,4		104	
α-Pinene	4,2; 2,5		104	
Decane	4,2		104	
Ethylene oxide				
Propylene oxide	3,6		103	
Hexanal	3,5		98	

Table 7 — Precision and storage recovery of solvents on Tenax sorbent tubes

Organic compound	Loading mg	$t = 0$ % CV <sup>a,c</sup>	$t = 5$ months		$t = 11$ months	
			Mean recovery <sup>b</sup>	% CV <sup>c</sup>	Mean recovery <sup>b</sup>	% CV <sup>c</sup>
<b>Hydrocarbons</b>						
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
<i>p</i> -Xylene	5,3	2,5	99,9	1,7	99,8	0,7
<i>o</i> -Xylene	11,0	2,4	100,0	1,7	98,8	0,7
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
<i>m</i> - + <i>p</i> -Ethyltoluene	10,5	2,3	98,8	1,7	96,9	1,2
<i>o</i> -Ethyltoluene	5,4	2,2	100,1	1,6	98,9	0,7
1,2,4-Trimethylbenzene	10,8	2,2	100,1	1,3	99,1	0,5
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
<b>Esters and glycol ethers</b>						
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

Table 7 (continued)

Organic compound	Loading mg	$t = 0$ % CV <sup>a,c</sup>	$t = 5$ months		$t = 11$ months	
			Mean recovery <sup>b</sup>	% CV <sup>c</sup>	Mean recovery <sup>b</sup>	% CV <sup>c</sup>
<b>Ketones</b>						
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
<b>Alcohols</b>						
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
<p><sup>a</sup> 6 replicates</p> <p><sup>b</sup> Normalized to toluene = 100. The stability of toluene has been established in a BCR (Bureau Communautaire de Référence) intercomparison [17].</p> <p><sup>c</sup> CV = coefficient of variation.</p>						

Table 8 — Blank levels for benzene, toluene and xylene for Chromosorb 106 and Carbograph TD-1

Study No.		Chromosorb 106			Carbograph TD-1		
		Benzene ng	Toluene ng	Xylene ng	Benzene ng	Toluene ng	Xylene ng
1) UK survey	Mean	7,69	1,39	3,23	7,22	2,04	5,59
	± standard deviation	1,96	0,55	1,64	2,75	0,78	2,28
	$n$	20	20	20	18	19	19
2) VOC air comparison	Mean	10,38	3,26	1,46	6,88	3,34	2,35
	± standard deviation	2,28	2,55	1,44	2,70	1,3	1,39
	$n$	14	14	14	14	14	14
3) World survey	Mean	5,63	2,09	0,96	2,61	4,39	1,63
	± standard deviation	3,04	2,36	0,51	1,13	6,19	1,17
	$n$	16	16	16	16	16	16

## Annex A (informative)

### Operating principles of diffusive sampling

#### A.1 Principles

A general overview is given in reference [27].

The mass of the analyte which can diffuse to a suitable sorbent within a certain time is determined by Equation (A.1), which is derived from Fick's First Law of diffusion:

$$m_s = \frac{A \cdot D \cdot (\rho_1 - \rho_2) \cdot t}{l} \quad (\text{A.1})$$

where

- $A$  is the area of the cross-section;
- $D$  is the diffusion coefficient;
- $\rho_1$  is the concentration of analyte at the diffusion cap;
- $\rho_2$  is the concentration of analyte at the sorbent bed;
- $m_s$  is the mass of analyte;
- $l$  is the length of surface of the sorbent to the diffusion cap;
- $t$  is the time.

Equation (A.1) refers to the situation in which  $\rho_2$  may be non-zero. Ideally  $\rho_1$  is equal to the concentration of the given analyte in the air outside the diffusive sampler and  $\rho_2$  equals zero ("zero sink"-condition). In that case the magnitude of the diffusive uptake rate,  $A \times D/l$  [see also Equation (A.2)], is dependent only on the diffusion coefficient of the given analyte and on the geometry of the diffusive sampler used (see Figure A.1).

The inlet of a sampler with cross-section  $A$  at position 1 defines the beginning of the diffusion path of an analyte with a concentration of  $\rho_1$ . A sorbent (S) at position 2, which will reduce the concentration of the analyte,  $\rho_2$ , to zero (ideally) due to sorption or chemical reaction, serves as the driving force for the diffusion along  $l$ .

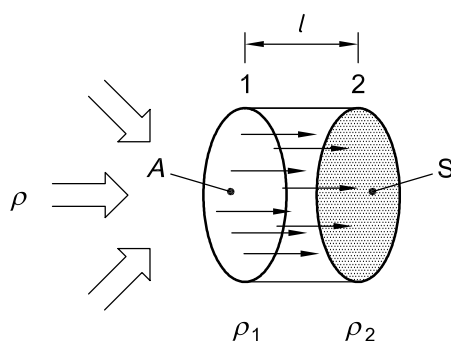


Figure A.1 — Schematic principle of diffusive sampling

## A.2 Dimensions of diffusive uptake rate

For a given mass concentration  $\rho$ , in micrograms per cubic metre of gas or vapour, the diffusive uptake rate  $q_V$  is given by:

$$q_V = \frac{m_s}{\rho \cdot t} \quad (\text{A.2})$$

where

$m_s$  is the mass of analyte in question, in picograms;

$t$  is the exposure time, in minutes.

NOTE 1 Although the uptake rate,  $q_V$ , has dimensions of cubic centimetres per minute, this is really a reduction of picograms per microgram per cubic metre per minute,  $\text{pg} \cdot (\mu\text{g}/\text{m}^3)^{-1} \cdot \text{min}^{-1}$ , and does not indicate a real volumetric flowrate of (analyte in) air.

NOTE 2 Diffusive uptake rates are very often quoted in units of  $\text{pg} \cdot \text{ppb}^{-1} \cdot \text{min}^{-1}$ . These are practical units, since most environmental analysts use parts per billion ( $\text{ppb}^3$ ) for concentrations of gases and vapours. The dependency of uptake rates on temperature and pressure is explained later (A.4.1). Thus for a given concentration (of gas or vapour), the uptake rate in  $\text{ppb}$  is given by:

$$q_{V'} = \frac{m_s}{\varphi_1 \cdot t} \quad (\text{A.3})$$

where

$\varphi_1$  is the volume fraction  $\times 10^{-9}$ .

NOTE 3 Ideal and practical diffusive uptake rates are related by Equation (A.4) [see also Equation (4)]:

$$q_{V'} = \frac{q_V \cdot m \cdot 293 \cdot p}{24,0 \cdot T \cdot 101} \quad (\text{A.4})$$

## A.3 Bias due to the selection of a non-ideal sorbent

The performance of a diffusive sampler depends critically on the selection and use of a sorbent or collection medium which has high sorption efficiency. The residual vapour pressure of the sampled compound at the sorbent surface ( $\rho_2$ ) will then be very small in comparison to the ambient concentration, and the observed uptake rate will be close to its ideal steady-state value, which can usually be calculated from the geometry of the sampler and the diffusion coefficient of the analyte in air.

In the case where a weak sorbent is used, then  $\rho_2$  in Equation (A.1) is non-zero, and  $m_s$  will decrease with the time of sampling. Hence  $q_V$  in Equation (A.2) will also decrease with the time of sampling. The magnitude of this effect is dependent on the adsorption isotherm of the analyte and sorbent concerned, and may be calculated with the aid of computer models [28, 29].

Another manifestation of the same effect is back-diffusion, sometimes called reverse diffusion. This can happen if, some time after sampling has started, the vapour pressure of the analyte at the sorbent surface,  $\rho_2$ , is greater than the external concentration,  $\rho_1$ , for example if a sampler is first exposed to a high concentration and then to a much lower or even zero concentration. This type of exposure profile can occur in certain applications, and the magnitude of any error introduced depends on whether the period of high concentration

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3)  $\text{ppb}$  are units deprecated by ISO. The correct unit here is volume fraction,  $\varphi$ ,  $\times 10^{-9}$ .

occurs at the beginning, middle or end of the sampling period. The phenomenon has been discussed in references [30], [31] and [32], and a simple test is proposed<sup>[33]</sup> to give an estimate of the maximum bias to be expected between a pulsed exposure and an exposure to a constant concentration, which latter normally provides the basis for the sampler calibration. This test is 30 min exposure to a high concentration, followed by 7,5 h of clean air, and has been adopted in EN 838. For ambient air applications, however, it is considered that an exposure profile of alternate periods of high and low exposure [e.g. 12 h at 2 LV (limit value) followed by 12 h at zero concentration alternately for 7 days] is more typical of the intended application, where diurnal variations in concentration are common. The extent of back-diffusion can also be modelled theoretically<sup>[29], [34]</sup>.

## A.4 Environmental factors affecting sampler performance

### A.4.1 Temperature and pressure

From Maxwell's equation, the diffusion coefficient,  $D$ , is a function of absolute temperature and pressure:

$$D = f(T^{3/2}, p^{-1}) \quad (\text{A.5})$$

But from the general gas law:

$$pV = nRT \quad (\text{A.6})$$

$$c = n/V = p/RT \quad (\text{A.7})$$

where

$n$  is the number of moles;

$R$  is the gas constant.

Substituting Equations (A.5) and (A.6) in (A.1), we get:

$$\begin{aligned} m_s &= f(p/T, T^{3/2}/p) \\ &= f(T^{1/2}) \end{aligned} \quad (\text{A.8})$$

Thus,  $m_s$  is independent of pressure, but dependent on the square root of absolute temperature, i.e. increasing about 0,2 % per degree Celsius.

If a weak sorbent is used, temperature can also affect the sorption capacity, which will reduce the mass collected slightly. For example, the uptake rate of benzene collected on Tenax reduces slightly in the range 20 °C to 60 °C from 1,33 ng·ppm<sup>-1</sup>·min<sup>-1</sup> to 1,23 ng·ppm<sup>-1</sup>·min<sup>-1</sup> fraction by volume<sup>[35]</sup>.

### A.4.2 Humidity

High humidity can affect the sorption capacity of hydrophilic sorbents, such as charcoal and Molecular Sieve. This normally reduces the sampling time (at a given concentration) before saturation of the sorbent occurs, when sampling becomes non-linear because of a significant  $\rho_2$  term in Equation (A.1). High humidity can also alter the sorption behaviour of the exposed inner wall of tube-type samplers, particularly if condensation occurs.

### A.4.3 Transients

Simple derivations of Fick's Law assume steady-state conditions, but in the practical use of diffusive samplers, the ambient level of pollutants is likely to vary widely. The question then arises whether a sampler will give a truly integrated response (ignoring sorbent effects, see A.4.1) or will "miss" short-lived transients before they have had a chance to be trapped by the sorbent. The problem has been discussed



theoretically [30], [35], [36], [37] and practically [35], [38], [39] and shown not to be a problem, provided the total sampling time is well in excess of (say 10 times) the time constant of the diffusive sampler, i.e. the time a molecule takes to diffuse into the sampler under steady-state conditions. The time constant,  $\tau$ , for most commercial samplers is between about 1 s and 10 s.  $\tau$  is given by:

$$\tau = l^R / D$$

#### A.4.4 Air velocity

##### A.4.4.1 Effect of low and high wind speeds

Ambient air face velocity and orientation can affect the performance of a diffusive sampler because they can influence the effective diffusion path length [40], [41], [42], [43]. The diffusive mass uptake of a sampler [Equation (A.1)] is a function of the length,  $l$ , and the cross-sectional area,  $A$ , of the diffusion gap within the sampler. The nominal diffusion path length is defined by the geometry of the sampler and is the distance between the sorbent surface and the external face of the sampler. The cross-sectional area is also defined by the geometry of the sampler and if the cross-section of the diffusion gap is not constant along its length, is defined by the narrowest portion. The effective length,  $l$ , is not necessarily the same as the nominal length, and may be greater or less, depending on circumstances.

Under conditions of low external wind speeds, the effective diffusion path length may be increased [42], [43]. This is because a “boundary layer” [40], [41] exists between the stagnant air within the sampler and the turbulent air outside which contributes to the effective diffusion path length,  $l$ . In reality, there is an area outside the sampler where there is a transition between static air and turbulent air, but this is equivalent to an extra length ( $\delta l$ ) of static air which shall be included in the value of  $l$ . The value of  $\delta l$  depends on the external geometry of the sampler, being roughly proportional to the linear cross-section of the sampler collection surface. It also decreases with increasing air velocity. Its significance depends on the value of the nominal path length of the diffusive sampler. Thus a sampler with a small cross-section and long internal air gap will be relatively unaffected by air velocity, whilst a short, fat sampler will be significantly affected. This is borne out in practice, as has been demonstrated with samplers of varying length [42], [43]. Low uptake rates are observed at low air velocities, but increase to a plateau value as the boundary layer effect becomes insignificant.

Under conditions of high external wind speeds, the effective diffusion path length may be decreased [42], [44], [45], [46], [47], [48]. This is because turbulent air disturbs the static air layer within the sampler, which reduces the effective air gap by a factor  $\delta l$ . The value of  $\delta l$  is small, provided the length-to-diameter ratio of the sampler air gap is greater than 2,5 to 3 [42], or it can be avoided or greatly reduced by incorporating a draught shield, e.g. a stainless steel screen or plastic membrane [47], [48].

The overall effect is therefore sinusoidal.

##### A.4.4.2 Consequences for different sampler geometries

Tube-type samplers are typically unaffected by low air velocities [35], [49], [50] but those without a draught shield may be affected by high speeds.

#### A.4.5 Transportation

Most samplers require transportation between the sampling site and an analytical laboratory, so that it is important that sample integrity be maintained during this process. The following precautions are recommended.

- a) Ensure that any seals are sufficiently tight to avoid ingress of contamination or loss of sample during transit: metal-plastic seals may become loose if a large temperature change occurs.
- b) Place the samplers in inert closed containers to minimize the ingress of external contamination.
- c) If air-freighting samples, ensure that they are not subjected to negative pressure, e.g. in the baggage hold.

- d) Avoid exposure to high temperatures during transit, e.g. in the boot of a car.
- e) If possible, keep the samplers at low temperature and away from contamination sources e.g. petroleum or aviation fuel, but avoiding condensation on the sample.

Ensure that adequate sample blanks are transported with the samples so that any of the above problems can be identified.

## A.5 Protection from adverse environmental conditions

### A.5.1 General

In practical use in the ambient environment, attention shall be paid to three main considerations; air velocity, protection from precipitation, and security. Data with suggested distances to the walls, doors and windows as well as for the minimum and maximum sampling heights are given in prEN 13528-3.

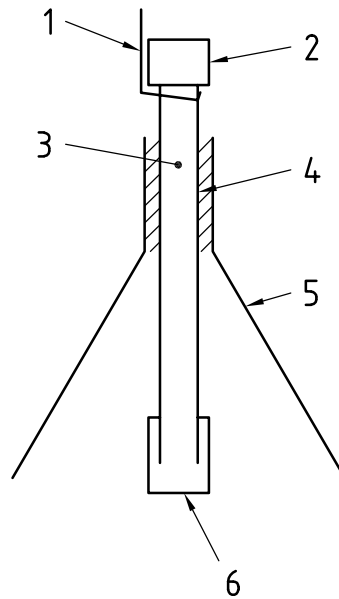
### A.5.2 Air velocity

The potential effect of air velocity is described in A.4.4. Low air velocities are most likely to be found indoors, where typical levels, without forced ventilation, are about 10 cm/s<sup>[49]</sup>, <sup>[51]</sup>. Monthly averaged ambient wind velocities in Europe are mostly in the range 1 m/s to 10 m/s<sup>[52]</sup> but can fall below 0,5 m/s temporarily in the case of stable meteorological conditions (inversions) and/or locally in valleys of mountainous areas <sup>[53]</sup>, <sup>[54]</sup>. Moreover, at least for local source emissions, pollutant concentrations are inversely proportional to wind speed <sup>[52]</sup> so any sampling error at low wind speeds would be magnified in the time-weighted average.

In indoor locations with low air movement (e.g. 5 cm/s to 10 cm/s), the sampler has been shown to perform as designed. In outdoor locations, precipitation, direct solar heating and high wind velocities may adversely affect the performance of the sampler; therefore, it should be protected by a shelter <sup>[57]</sup>, <sup>[58]</sup>.

### A.5.3 Protection from precipitation

Protection from precipitation is important for all types of sampler. Rain or melted snow can block the sampling surfaces<sup>[55]</sup>, particularly of tube samplers oriented vertically downwards (which is the usual position to avoid ingress of particulates). A simple shelter for a tube-type sampler may consist of an inverted plastic funnel located such that the tube fits snugly into the spout of the funnel (cut short if necessary) and the open end of the tube is just visible below the funnel opening<sup>[56]</sup>. This example is illustrated in Figure A.2. Another possibility is an inert "nest box", with holes drilled in the bottom. The tube(s) are placed inside the box, again with the open end of the tube just visible below the opening.



#### Key

- 1 string (thread)
- 2 screw-fit cap
- 3 sorbent
- 4 sample tube
- 5 funnel
- 6 diffusion cap with gauze in end

**Figure A.2 — Sampling tube with protective weather hood**

An alternative to providing a shelter is to modify the diffusive sampler. For example, the diffusion end cap of a tube-type sampler can be modified with the addition of an aluminium brim to prevent rainwater blocking the diffusion surface<sup>[25]</sup>. However, such an arrangement can modify the performance characteristics of the sampler with respect to the minimum air velocity requirement.

#### A.5.4 Security

Security is also a major consideration, as samplers exposed for long periods in public or semi-public places are subject to theft and vandalism. Samplers should be sited, so far as possible, out of reach, inconspicuous and/or designed to look like something else, e.g. the nestbox idea.

## Annex B (informative)

### Description of sorbent types

Sorbent	Type
Ambersorb XAD-4	Styrene/divinylbenzene copolymer
Carbotrap B/C	Graphitized carbon
Carbopack B/C	Graphitized carbon
Carbosieve S-III	Carbon molecular sieve
Carboxen 569	Carbon molecular sieve
Carboxen 1000	Carbon molecular sieve
Chromosorb 102	Styrene/divinylbenzene
Chromosorb 106	Polystyrene
Carbograph TD-1	Graphitized carbon
Porapak N	Vinylpyrrolidone
Porapak Q	Ethylvinylbenzene/divinylbenzene
Spherocarb	Carbon molecular sieve
Tenax TA	Poly(2,6-diphenyl- <i>p</i> -phenylene oxide)
Tenax GR	Graphitized poly(diphenylene oxide)

NOTE Carbotrap<sup>TM</sup>, Carbopack<sup>TM</sup>, Carbosieve SIII<sup>TM</sup> and Carboxen<sup>TM</sup> are the trade names of products supplied by Supelco, Inc., USA; Tenax<sup>TM</sup> is a trademark of Enka Research Institute, NV, NL; Chromosorb<sup>TM</sup> is the trade name of a product supplied by Manville Corp, USA; Porapak<sup>TM</sup> is the trade name of a product supplied by Waters Associates Inc., USA; Spherocarb<sup>TM</sup> is the trade name of a product supplied by Analabs Inc., USA; Ambersorb<sup>TM</sup> is the trade name of a product supplied by Rohm & Haas Co., USA; Carbograph<sup>TM</sup> is the trade name of a product supplied by Alltech Associated, USA. This information is given for the convenience of users of this part of ISO 16017 and does not constitute an endorsement by ISO of the products named. Equivalent products may be used if they can be shown to lead to the same results.

## Annex C (informative)

### Guidance on sorbent selection

Table C.1

Sample tube sorbent	Approx. analyte volatility range	Max. temp. °C	Specific surface area m <sup>2</sup> /g	Examples of analytes
Carbotrap™ C Carbopack™ C	n-C <sub>8</sub> to n-C <sub>20</sub>	> 400	12	Alkyl benzenes and aliphatics ranging in volatility from n-C <sub>8</sub> to n-C <sub>16</sub> .
Tenax™ TA	b.p. 100 °C to 400 °C n-C <sub>6</sub> to n-C <sub>26</sub>	350	35	Aromatics, non-polar components (b.p. <sup>c</sup> > 100 °C) and less volatile polar components (b.p. > 150 °C).
Tenax GR	b.p. 100 °C to 450 °C n-C <sub>7</sub> to n-C <sub>30</sub>	350	35	Alkyl benzenes, vapour phase PAHs and PCBs and as above for Tenax TA.
Carbotrap B Carbograph TD-1 Carbopack B	(n-C <sub>4</sub> ) n-C <sub>5</sub> to n-C <sub>14</sub>	> 400	100	Wide range of VOCs including ketones, alcohols, and aldehydes (b.p. > 75 °C) and all non-polar compounds within the volatility range specified. Plus perfluorocarbon tracer gases.
Chromosorb™ 102	b.p. 50 °C to 200 °C	250	350	Suits a wide range of VOCs, including oxygenated compounds and haloforms less volatile than methylene chloride.
Chromosorb 106	b.p. 50 °C to 200 °C	250	750	Suits a wide range of VOCs, including hydrocarbons from n-C <sub>5</sub> to n-C <sub>12</sub> . Also good for volatile oxygenated compounds.
Porapak™ Q	b.p. 50 °C to 200 °C n-C <sub>5</sub> to n-C <sub>12</sub>	250	550	Suits a wide range of VOCs including oxygenated compounds.
Porapak N	b.p. 50 °C to 150 °C n-C <sub>5</sub> to n-C <sub>8</sub>	180	300	Specifically selected for volatile nitriles; acrylonitrile, acetonitrile and propionitrile. Also good for pyridine, volatile alcohols from EtOH, MEK, etc.
Spherocarb™ a	- 30 °C to 150 °C C <sub>3</sub> to n-C <sub>8</sub>	> 400	1 200	Good for very volatile compounds such as VCM, ethylene oxide, CS <sub>2</sub> and CH <sub>2</sub> Cl <sub>2</sub> . Also good for volatile polars, e.g. MeOH, EtOH and acetone.
Carbosieve™ SIII <sup>a</sup> or Carboxen™1000 <sup>a</sup>	- 60 °C to 80 °C	400	800	Good for ultra-volatile compounds such as C <sub>3</sub> -, C <sub>4</sub> -hydrocarbons, volatile haloforms and freons.
Molecular Sieve <sup>b</sup>	- 60 °C to 80 °C	350		Used specifically for 1,3-butadiene and nitrous oxide.

NOTE Trademark designations are given in Annex B.

<sup>a</sup> These sorbents exhibit some water retention. Safe sampling volumes should be reduced by a factor of 10 if sampling at high (> 90 %) relative humidity.

<sup>b</sup> Significantly hydrophilic. Do not use in high humidity atmospheres unless special precautions are taken.

<sup>c</sup> b.p. = boiling point.

## Annex D (informative)

### Guidance on sorbent use

Table D.1

Sample tube sorbent	Maximum temp. °C	Hydrophobic	Temp. and gas flowrate for conditioning <sup>a</sup>	Temp. and min. gas flowrate for desorption	Recommended cold trap packing
Carbotrap C Carbopack C	> 400	Yes	350 °C and 100 ml/min	325 °C and 30 ml/min	Tenax or Carbopack C
Tenax TA	350	Yes	330 °C and 100 ml/min	300 °C and 30 ml/min	Tenax
Tenax GR	350	Yes	330 °C and 100 ml/min	300 °C and 30 ml/min	Tenax
Carbotrap B Carbopack	> 400	Yes	350 °C and 100 ml/min	325 °C and 30 ml/min	Tenax or Carbopack B
Chromosorb 102	250	Yes	250 °C and 100 ml/min	225 °C and 30 ml/min	Dual-bed Carbopack B plus carbon molecular sieve or Chromosorb 102
Chromosorb 106	250	Yes	250 °C and 100 ml/min	250 °C and 30 ml/min	Dual-bed Carbopack B plus carbon molecular sieve or Chromosorb 106
Porapak Q	250	Yes	250 °C and 100 ml/min	225 °C and 30 ml/min	Dual-bed Carbopack B plus carbon molecular sieve or Porapak Q
Porapak N	180	Yes	180 °C and 100 ml/min	180 °C and 30 ml/min	Dual-bed Carbopack B plus carbon molecular sieve or Porapak N
Spherocarb <sup>b</sup>	> 400	No	400 °C and 100 ml/min	390 °C and 30 ml/min	Dual-bed Carbopack B plus carbon molecular sieve or Spherocarb
Carbon molecular sieve such as Carbosieve S-III <sup>b</sup> or Carboxen 1000 <sup>b</sup>	400	No	350 °C and 100 ml/min	325 °C and 30 ml/min	Dual-bed Carbopack B plus carbon molecular sieve or carbon molecular sieve alone
Molecular sieve <sup>c</sup>	350	No	330 °C and 100 ml/min	300 °C and 30 ml/min	Dual-bed Carbopack B plus carbon molecular sieve or carbon molecular sieve alone
Tenax / Carbopack B combination tube type	350	Yes	330 °C and 100 ml/min	300 °C and 30 ml/min	Tenax
Carbopack B / Carbon molecular sieve <sup>b</sup> combination tube type	400	No	350 °C and 100 ml/min	325 °C and 30 ml/min	Dual-bed Carbopack B plus carbon molecular sieve
Carboxen 1000 series, combination tube type	400	No	350 °C and 100 ml/min	325 °C and 30 ml/min	Dual-bed Carbopack B plus carbon molecular sieve

NOTE Trademark designations are given in Annex B.

<sup>a</sup> The conditioning temperature is not the same as the pre-conditioning temperature (see 4.3).

<sup>b</sup> These sorbents exhibit some water retention. Safe sampling volumes should be reduced by a factor of 10 if sampling at high (> 90 %) relative humidity.

<sup>c</sup> Significantly hydrophilic. Do not use in high humidity atmospheres unless special precautions are taken.

## Annex E (informative)

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

#### E.1 Data on overall uncertainty

Laboratory tests of the procedure, following EN 838<sup>[4]</sup> and using a diffusive tube as specified in 5.1 containing an appropriate sorbent, yielded diffusive uptake rates for individual organic compounds as given in Table 1. Laboratory and field test of the procedure, following EN 13528-2<sup>[5]</sup> and using a diffusive tube as specified in 5.1 containing an appropriate sorbent, yielded diffusive uptake rates for individual organic compounds as given in Table 2. There was no silicone membrane in the diffusion cap. Results with a silicone membrane are about 10 % lower. In many cases, different values apply to workplace monitoring over short periods than to ambient and indoor measurements over longer sampling periods. The results of these evaluations are from a variety of sources. For Table 1 they are summarized in reference [10]. For Table 2, source references are listed in that Table. Different uptake rates may be given by other makes of diffusive tube, or if a membrane is employed, or if a different sorbent is used, but the general performance of other systems is expected to be similar to that described here (see 8.6).

Blank levels of benzene, toluene and xylene have been determined<sup>[11]</sup> on unspiked, conditioned tubes as specified in 5.1 and Clause 6, and 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. Results of Chromosorb 106 and Carbograph TD-1 are given in Table 8. For both sorbents, recoveries were in the low nanogram range, slightly higher than indicated in reference [1] for freshly-conditioned Carbograph.

#### E.2 Data on precision and bias

A summary of existing data on laboratory tests using tubes as specified in 5.1 is presented.

Laboratory tests<sup>[2]</sup> indicated within-batch repeatability (expressed as a coefficient of variation,  $\sigma_{n-1}$ , six replicates) of between 0,5 % to 2 % for 14 representative VOCs including aromatic hydrocarbons, chlorinated hydrocarbons, ketones, esters and glycol ethers, sampled on either Tenax or Chromosorb 106. Diffusive samples were taken from a reference atmosphere generated with an overall uncertainty of better than 3 %. Between-batch variability (i.e. taking account of different conditions of exposure times over a range of two to four hours and concentrations in the range of 0,5 to 2,0 Limit Values (LV)) was between 2 % and 12 %. The variability depending on the compound, reflecting a small change in the uptake rate with exposure conditions: the higher values being obtained when the sorbent/analyte combination was non-ideal. The between-batch values equate to an overall uncertainty of between 6 % and 24 %.

Laboratory tests<sup>[11]</sup> on tubes liquid-spiked with benzene, toluene and xylene at 80 ng or 200 ng levels are summarized in Table 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.

Field tests<sup>[11]</sup> at a number of UK sites at which benzene, toluene and xylene were measured at ambient mass concentrations of between  $1 \mu\text{g}/\text{m}^3$  and  $10 \mu\text{g}/\text{m}^3$  by diffusive tubes and fixed monitoring hydrocarbon analysers indicated that the mean precision of the diffusive method was 11 % for the benzene determination, 7 % for toluene and 5 % for xylene, expressed as a coefficient of variation ( $n = 4$ ; two Chromosorb 106 tubes and two Carbograph tubes exposed over a four-week period). The full results are given in Table 4. The VOC air data should be taken as indicative only, due to low data coverage during the corresponding diffusive sampling period. In a similar field test<sup>[11]</sup> at a number of world sites (Table 5), excluding Brazil, the mean

precision of the diffusive method was 11 % for the benzene determination, 8 % for toluene and 6 % for xylene, expressed as a coefficient of variation.

In a field test <sup>[12]</sup> at a single UK site at which benzene was measured at ambient mass concentrations of between < 1 mg/m<sup>3</sup> to 2,5 mg/m<sup>3</sup> by both diffusive tubes and a fixed monitoring hydrocarbon analyser, the annual running average given by the fixed instrument was 1,95 mg/m<sup>3</sup> compared to 1,76 mg/m<sup>3</sup> using diffusive tubes.

Where Table 1 lists results at Level A or B, then the overall uncertainty as defined in EN 482<sup>[13]</sup> was better than 30 %. For the data in Table 2, the overall uncertainty as defined in EN 13528-1<sup>[14]</sup> is expected to be better than 30 %.

NOTE For workplace measurements (Table 1), Level A is a full validation according to EN 838<sup>[4]</sup>. Level 1A, i.e. 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 1 is a partial validation (where not all of the tests in EN 838 have been undertaken) allowed on a temporary basis by EN 482. For ambient measurements (Table 2) full validations according to EN 13528-2<sup>[5]</sup> require both laboratory and field testing and for none of the data in Table 2 has a full evaluation been conducted. There is no equivalent to level B allowed in EN 13528-1. Nevertheless, from the data above, the field precision of environmental sampling may be expected to be in the range 5 % to 11 % and the reproducibility of the uptake rate determination (Table 4) is about 10 %. The combined precision is therefore about 15 % and the resulting overall uncertainty 30 %.

### **E.3 Data on storage**

A summary of existing data on laboratory storage tests using tubes as specified in 5.1 is presented in Tables 6 and 7.

Laboratory tests<sup>[15]</sup> on tubes liquid-spiked with a limited range of compounds on Chromosorb 106 and Carboxen 569 at a load level of approximately 1,0 µg and stored at room temperature for two weeks are summarized in Table 6. The mean recovery (relative to unstored tubes) for Chromosorb 106 was 105,6 %.

Laboratory tests<sup>[16]</sup> on tubes liquid-spiked with a broader range of compounds on Tenax TA at a single load level of approximately 10 µg and stored at room temperature for 5 months are summarized in Table 7. Excluding hexane and methoxyethanol, the mean recovery (relative to unstored tubes) was 99,7 % and the mean coefficient of variation ( $\sigma_{n-1}$ ) 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 coefficient of variation was 0,9 %.

During the certification of CRM 112<sup>[17]</sup>, the stability of a batch of tubes charged with benzene, toluene and *m*-xylene was examined for up to 25 months at temperatures between 0 °C and 40 °C. After 14 months and storage at 0 °C to 4 °C, recoveries of the three compounds were 101 % to 103 %. Under the same conditions but at ambient temperature and at 40 °C, recoveries were respectively 102 % to 104 % and 100 % to 104 %. No instability was detected after 25 months, but recoveries were not reported.

Seals may become loose during refrigeration because of differential thermal contraction. To avoid loss of sample or ingress of external contamination, check the seals periodically. Refrigeration can assist to reduce any cross-reaction of sorbed VOCs.



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