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

Part 1: Pumped sampling

The European Standard EN ISO 16017-1:2000 has the status of a
British Standard

ICS 13.040.20; 13.040.30

National foreword

This British Standard is the official English language version of EN ISO 16017-1:2000. It is identical with ISO 16017-1:2000.

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 committee can be obtained on request to its secretary.

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the BSI Standards Catalogue under the section entitled “International Standards Correspondence Index”, or by using the “Find” facility of the BSI Standards Electronic Catalogue.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, the EN ISO title page, the EN ISO foreword page, the ISO title page, pages ii to iv, pages 1 to 28, an inside back cover and a back cover.

The BSI copyright date displayed in this document indicates when the document was last issued.

Amendments issued since publication

Amd. No.	Date	Comments

This British Standard, having been prepared under the direction of the Health and Environment Sector and policy Committee, was published under the authority of the Standards Policy and Strategy Committee on 21 September 2001

ICS

English version

Indoor, ambient and workplace air - Sampling and analysis of
volatile organic compounds by sorbent tube/thermal
desorption/capillary gas chromatography - Part 1: Pumped
sampling (ISO 16017-1:2000)

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 1: Echantillonnage par pompage (ISO
16017-1:2000)

Innenraumluft, Außenluft und Luft am Arbeitsplatz -
Probenahme und Analyse flüchtiger organischer
Verbindungen durch Sorptionsröhrchen/thermische
Desorption/Kapillar-Gaschromatographie - Teil 1:
Probenahme mit einer Pumpe (ISO 16017-1:2000)

This European Standard was approved by CEN on 30 September 2000.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Management Centre or to any CEN member.

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.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.



EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

Foreword

The text of the International Standard ISO 16017-1:2000 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 May 2001, and conflicting national standards shall be withdrawn at the latest by May 2001.

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, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

NOTE FROM CMC: The foreword is susceptible to be amended on reception of the German language version. The confirmed or amended foreword, and when appropriate, the normative annex ZA for the references to international publications with their relevant European publications will be circulated with the German version.

Endorsement notice

The text of the International Standard ISO 16017-1:2000 was approved by CEN as a

European Standard without any modification.

INTERNATIONAL STANDARD

ISO 16017-1

First edition
2000-11-15

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

Part 1: Pumped 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 1: Échantillonnage par pompage

Reference number
ISO 16017-1:2000(E)



Contents

Page

Foreword.....	iv
1 Scope	1
2 Normative references	2
3 Terms and definitions	2
4 Principle.....	3
5 Reagents and materials	3
6 Apparatus	5
7 Sample tube conditioning.....	6
8 Calibration of pump.....	7
9 Sampling.....	7
10 Procedure	8
10.1 Safety precautions.....	8
10.2 Desorption and analysis	8
10.3 Calibration	9
10.4 Determination of sample concentration.....	10
10.5 Determination of desorption efficiency.....	10
11 Calculations.....	10
11.1 Mass concentration of analyte	10
11.2 Volume concentration of analyte	11
12 Interferences	11
13 Performance characteristics	11
14 Test report	12
15 Quality control.....	12
Annex A (normative) Determination of breakthrough volumes from gas standards.....	21
Annex B (normative) Determination of breakthrough volume from the extrapolated retention volume.....	22
Annex C (informative) Description of sorbent types	23
Annex D (informative) Guidance on sorbent selection	24
Annex E (informative) Guidance on sorbent use.....	25
Annex F (informative) Summary of data on overall uncertainty, precision, bias and storage.....	26
Bibliography.....	28

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 3.

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 part of ISO 16017 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 16017-1 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*.

$\frac{3}{4}$ *Part 1: Pumped sampling*

$\frac{3}{4}$ *Part 2: Diffusive sampling*

Annexes A and B form a normative part of this part of ISO 16017. Annexes C through F are for information only.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 16017. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 16017 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*.

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*.

ISO 6141:2000, *Gas analysis — Requirements for certificates for calibration gases and gas mixtures*.

ISO 6145-1:1986, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 1: Methods of calibration*.

ISO 6145-3:1986, *Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 3: Periodic injections into a flowing gas stream*.

ISO 6145-4:1986, *Gas analysis — Preparation of calibration gas mixtures — Dynamic volumetric methods — Part 4: Continuous injection method*.

ISO 6145-5:—²⁾, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 5: Capillary calibration devices*.

ISO 6145-6:—²⁾, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 6: Critical orifices*.

ISO 6349:1979, *Gas analysis — Preparation of calibration gas mixtures — Permeation method*.

EN 1076:1997, *Workplace atmospheres — Pumped sorbent tubes for the determination of gases and vapours — Requirements and test methods*.

3 Terms and definitions

For the purposes of this part of ISO 16017, the following terms and definitions apply.

3.1

breakthrough volume

volume of test atmosphere that can be passed through a sorbent tube before the concentration of eluting vapour reaches 5 % of the applied test concentration

NOTE 1 The breakthrough volume varies with the vapour and the sorbent type.

NOTE 2 See reference [4]. 3.2

retention volume

elution volume at peak maximum of a small aliquot of an organic vapour eluted from a sorbent tube by air or chromatographic carrier gas

2) To be published.

4 Principle

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 capillary column and a flame ionization detector or other suitable detector, where it is analysed. Analytical calibration is achieved by means of liquid or vapour spiking onto a sorbent tube.

5 Reagents and materials

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

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

5.1 Volatile organic compounds, for calibration purposes, using either liquid spiking (5.7 and 5.8) or vapour spiking (5.4 to 5.6) onto sorbent tubes.

5.2 Dilution solvent, for preparing calibration blend solution for liquid spiking (5.7). This should be of chromatographic quality. It shall be free from compounds co-eluting with the compound or compounds of interest (5.1).

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.

5.3 Sorbents, of recommended particle size 0,18 mm to 0,25 mm (60 to 80 mesh).

Each sorbent should be preconditioned under a flow of inert gas by heating it overnight (= 16 h) at a temperature at least 25 °C below the published maximum for that sorbent before packing the tubes. To prevent recontamination of the sorbents, 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 prepacked by the manufacturer are also available for most sorbents and as such only require conditioning.

NOTE 1 Sorbent particle sizes larger than 0,18 mm to 0,25 mm may be used but the breakthrough characteristics given in Tables 1 to 6 may be affected. Smaller sorbent particle size ranges are not recommended because of back-pressure problems.

NOTE 2 A description of sorbents is given in annex C and a guide for sorbent selection is given in annex D. Equivalent sorbents may be used. A guide to sorbent conditioning and analytical desorption parameters is given in annex E.

5.4 Calibration standards, preferably prepared by loading required amounts of the compounds of interest on sorbent tubes from standard atmospheres (see 5.5 and 5.6), 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 5.7 and 5.8), provided that the accuracy of the spiking technique is either:

- a) established by using procedures giving spiking levels fully traceable to primary standards of mass and/or volume, or,
- b) confirmed by comparison with reference materials, if available, standards produced using standard atmospheres, or results of reference measurement procedures.

NOTE The loading ranges given in 5.6, 5.7 and 5.8 are not mandatory and approximate to the application range given in clause 1 for a 2-litre sample. For specific applications in which larger volumes are used to measure lower concentrations, other loading ranges may be more appropriate.

5.5 Standard atmospheres.

Prepare standard atmospheres of known concentrations of the compound(s) of interest by a recognized procedure. Methods described in ISO 6141, the appropriate part of ISO 6145 and ISO 6349 are suitable. 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.

5.6 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 equivalent to 10 mg/m³ and 100 mg/m³. For workplace air, load sorbent tubes with 100 ml, 200 ml, 400 ml, 1 l, 2 l, or 4 l of the 10 mg/m³ 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 mg/m³ atmosphere.

5.7 Solutions for liquid spiking.

5.7.1 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 (5.2), stopper and shake to mix.

5.7.2 Solution 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 5.7.1. Make up to 100 ml with dilution solvent, stopper and shake to mix.

5.7.3 Solution containing approximately 100 mg/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 (5.2), stopper and shake to mix.

5.7.4 Solution containing approximately 10 mg/ml of liquid components.

Introduce 50 ml of dilution solvent into a 100 ml volumetric flask. Add 10 ml of solution described in 5.7.3. Make up to 100 ml with dilution solvent, stopper and shake to mix.

5.7.5 Solution containing approximately 1 mg/ml of gas components.

For gases, e.g. ethylene oxide, a high level calibration solution may 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, but correct for any non-ideality of the particular pure gas compound.

5.7.6 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, but correct for any non-ideality of the particular pure gas compound.

5.8 Standard sorbent tubes loaded by liquid spiking.

Prepare loaded sorbent tubes by injecting aliquots of standard solutions onto clean sorbent tubes as follows. Fit a sorbent tube into the injection unit (6.10) through which inert purge gas and a 1 µl to 4 µl aliquot of an appropriate standard solution, injected through the septum, are passed. After an appropriate time, disconnect and seal the tube. Prepare fresh standards with each batch of samples. For workplace air, load sorbent tubes with 1 µl to 5 µl of solutions 5.7.1, 5.7.2 or 5.7.5. For ambient and indoor air, load sorbent tubes with 1 µl to 5 µl of solutions 5.7.3, 5.7.4 or 5.7.6.

NOTE In the case of methanol, a purge gas flowrate of 100 ml/min and a 5 min purge time have been found to be appropriate to eliminate most of the solution solvent from the tube. If other dilution solvents are used, the conditions should be determined experimentally.

6 Apparatus

Use ordinary laboratory apparatus and the following.

6.1 Sorbent tubes, compatible with the thermal desorption apparatus to be used (6.9).

Typically, but not exclusively, sorbent tubes are constructed of stainless steel tubing, 6,3 mm (1/4 inch) OD, 5 mm ID and 90 mm long. Tubes of other dimensions may be used but the safe sampling volumes (SSV) given in Tables 1 to 6 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. One end of the tube is marked, for example by a scored ring about 10 mm from the sampling inlet end. The tubes are packed with one or more preconditioned sorbents (5.3) so that the sorbent bed will be within the desorber heated zone and a gap of at least 14 mm is retained at each end to minimize errors due to diffusive ingress at very low pump flowrates. Tubes contain between 200 mg and 1 000 mg sorbent, depending on sorbent density (typically about 250 mg porous polymer or 500 mg carbon molecular sieve or graphitized carbon). The sorbents are retained by stainless steel gauzes and/or unsilanized glass wool plugs. If more than one sorbent is used in a single tube, the sorbents should be arranged in order of increasing sorbent strength and separated by unsilanized glass wool, with the weakest sorbent nearest to the marked sampling inlet end of the tube.

Do not pack sorbents with widely different ($> 50\text{ }^{\circ}\text{C}$) maximum desorption temperatures into a single tube, or it will be impossible to condition or desorb the more stable sorbent(s) sufficiently thoroughly without causing degradation of the least stable sorbent(s).

6.2 Sorbent tube end caps.

The tubes shall be sealed according to the requirements of EN 1076:1997, subclause 5.6, or equivalent, e.g. with metal screw-cap fittings with polytetrafluoroethylene (PTFE) seals.

6.3 Sorbent tube unions.

Two sorbent tubes may be connected in series during sampling with metal screw-cap couplings with PTFE seals.

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

6.5 Sampling pump

The pump should fulfil the requirements of EN 1232 [10] or equivalent.

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

6.6 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.

Sampling tubes shall not be used with plastic or rubber tubing upstream of the sorbent. The use of such tubing may introduce contaminants or sorbed sampled VOCs.

6.7 Soap-bubble meter or other suitable device for calibrating pump.

The flow meter shall be traceably calibrated to a primary flow standard.

NOTE The use of an uncalibrated integral flow meter for the calibration of pump flowrates may result in systematic errors of several tens of percent.

6.8 Gas chromatograph, fitted with a flame ionization, 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.

The gas chromatograph shall have a capillary column capable of separating the analytes of interest from other components.

6.9 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 flowrate. 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 (10.2). The desorbed sample, contained in the purge gas, is routed to the gas chromatograph and capillary column via a heated transfer line.

6.10 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.

7 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 E). Typical conditioning time is 10 min with carrier gas flowrate of 100 ml/min. The carrier gas flow should be in a direction opposite to that used during sampling. 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 used for 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.

8 Calibration of pump

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

One end of the calibrated flow meter should be at atmospheric pressure to ensure proper operation.

9 Sampling

Select a sorbent tube (or tube combination) appropriate for the compound or mixture to be sampled. Guidance on suitable sorbents is given in annex D.

If more than one tube is to be used, prepare a tube assembly by joining the tubes with a union (6.3).

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.

When used for personal sampling, to minimize channelling the tube assembly should be mounted vertically in the breathing zone. The pump is attached as appropriate to minimize inconvenience. When used for fixed location sampling, a suitable sampling site is chosen.

Turn the pump on and adjust the flowrate 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 standard is between 1 litre and 10 litres. If the total sample is likely to exceed 1 mg (i.e. 1 mg on each tube), the sample volume shall be reduced accordingly, or overload may occur.

NOTE 1 Sampling efficiency is 100 % (quantitative), provided the sampling capacity of the sorbents is not exceeded. If this capacity is exceeded, breakthrough of vapour from the tube assembly will occur. The breakthrough volume may be measured by sampling from a standard vapour atmosphere, whilst monitoring the effluent air with a flame ionization or equivalent detector (a suitable method is described in annex A). Alternatively, instead of determining the breakthrough volume directly, the mathematically related retention volume may be determined. The retention volume is determined chromatographically at elevated temperatures and subsequent extrapolation to room temperature. A suitable method is described in annex B.

The breakthrough volume of porous polymers vary with ambient air temperature, reducing by a factor of about 2 for each 10 °C rise in temperature. It also varies with sampling flowrate, being reduced substantially at flowrates below 5 ml/min or above 500 ml/min. The breakthrough volumes of carbon molecular sieves are less affected by temperature and flowrate, but are substantially reduced at high concentrations of volatile organic vapour or high relative humidity. To allow a suitable margin of safety, a safe sampling volume (SSV) is defined such that it is a volume of not more than 70 % of the 5 %-breakthrough volume (see A.1.1 in annex A) or 50 % of the retention volume (see B.1 in annex B). Tables 1 to 6 give typical values for retention volumes and safe sampling volumes. These values have been determined by the chromatographic method (annex B).

NOTE 2 The safe sampling volumes in Tables 1 to 6 have been determined by the chromatographic method (annex B). Measurements by the direct method (annex A) [4] indicate that the chromatographic method is a reliable indication of the true breakthrough capacity except under conditions of high concentrations or very high humidity. These measurements [4] indicate that breakthrough volumes at high (80 %) humidity are about a factor of two lower for porous polymers and a factor of ten lower for carbonaceous sorbents than the low humidity value. If high concentrations [$> 300 \text{ mg/m}^3$ (100 ppm)] are also anticipated, the breakthrough volumes for carbonaceous sorbents should be further reduced by a factor of two.

If safe sampling volumes for compounds are estimated which are not listed in Table 1, this estimation is only possible for such compounds which are situated between the two listed compounds of homologues of a chemical group. In all other cases the safe sampling volume shall be tested experimentally with appropriate trials (e.g. similar sampling media in-line and separate analysis).

Note and record the times, temperature, flowrate 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 flowrate 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. The tubes should be uniquely labelled. 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, refrigerated sealed metal or glass container. If possible the sampler should be refrigerated during transportation.

Record air temperature and barometric pressure periodically during sampling if it is desired to express concentrations reduced to specific conditions (11.1).

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. Label these as blanks.

NOTE 3 Since this method uses thermal desorption, unless the TD apparatus has the facility to retrap the sample after analysis, there will generally only be one opportunity to analyse the sample. If the sample is important and the chance of overload and/or sample breakthrough is a possibility, a second sample at a lower flowrate should be taken.

10 Procedure

10.1 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.

10.2 Desorption and analysis

Place the sorbent tube in a compatible thermal desorption apparatus. Purge the air from the tube to avoid chromatographic artefacts arising from the thermal oxidation of the sorbent or gas chromatographic stationary phase. Then heat the tube to displace the organic vapours which are passed to the gas chromatograph by means of a carrier gas stream. The gas flow direction at this stage should be the reverse of that used during sampling, i.e. the marked end of the tube should be nearest the gas chromatograph column inlet. Typically the gas flowrate through the tube should be in the order of 30 ml/min to 50 ml/min for optimum desorption efficiency.

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. During the purge period, care should be taken to minimize heating of the tube.

The desorbed sample occupies a volume of several millilitres of gas, so that pre-concentration is essential prior to capillary GC analysis. This can 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, can be used to pre-concentrate 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 shall be completely eliminated from the sample tube prior to desorption in order to prevent ice formation blocking the capillary tubing and stopping the thermal desorption process.

NOTE 1 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 will typically be 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 temperature	250 °C to 325 °C
Desorption time	5 min to 15 min
Desorption flowrate	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.)

The desorption temperature depends on the analyte and the sorbent used. Recommendations are given in Tables 1 to 6, but the maximum desorption temperatures given in annexes D and E for particular sorbents should be respected. Due to their potential thermal instability, secondary and tertiary volatile amines and some polyhalogenated compounds having one or two carbon atoms, especially brominated compounds, may suffer some thermal degradation.

Set the sample flow path 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 flow path 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 will depend largely on which compounds, if any, are present that might interfere in the chromatographic analysis.

NOTE 2 Typical examples, as used to determine the data in Table 8, are 50 m \times 0,22 mm fused silica columns with thick-film (1 μ m to 5 μ m) dimethylsiloxane or a 50 m stationary phase of 7 % cyanopropyl, 7 % phenyl, 86 % methylsiloxane. 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 near 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 3 Lower split ratios are suitable for ambient (typically 1:1 to 10:1) and indoor and some workplace air measurements (typically 1:1 to 20:1); higher split ratios for most workplace air measurements (typically 100:1 to 1000:1).

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

10.3 Calibration

Analyse each sorbent tube standard (5.6 or 5.8) 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 5.7 or atmospheres 5.4.

NOTE If the calibration range is less than one order of magnitude, then it is not necessary to take logarithms of the data.

10.4 Determination of sample concentration

Analyse the samples and sample blanks as described for the calibration standards in 10.2. Determine the peak area and read from the calibration graph the mass of the analyte in the desorbed sample.

10.5 Determination of desorption efficiency

The efficiency of desorption should be checked by comparing the chromatographic response of a sorbent tube standard (10.3) 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 10.3, but using solutions 5.7 or atmosphere 5.6. This calibration should be the same or nearly the same as that in 10.3. 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.

NOTE 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 with that of n-hexane (5.1). 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 [3]. 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.

11 Calculations

11.1 Mass concentration of analyte

Calculate the concentration of the analyte in the sampled air, c_m , in micrograms per cubic metre, by means of equation (1):

$$c_m = \frac{m_F - m_B}{V} \times 1000 \quad (1)$$

where

m_F is the mass of analyte present in the actual sample as found in 6.3, in micrograms (sum of tubes if more than one used);

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

V is the volume of sample taken, in litres.

NOTE 1 If m_F and m_B are expressed in milligrams, the resultant concentration, c_m , will be in milligrams per cubic metre.

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

$$c_c = m_c \times \frac{101}{p} \times \frac{T + 273}{298} \quad (2)$$

where

c_c is the concentration of analyte in the 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.

11.2 Volume concentration of analyte

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

$$c_V = c_m \times \frac{24,5}{M} \times \frac{101}{p} \times \frac{T + 273}{298} \quad (3)$$

where

24,5 is the molar volume at 25 °C and 101 kPa;

M is the molecular mass of the analyte of interest, in grams per mole.

NOTE If c_m is expressed in milligrams per cubic metre, the resultant concentration, c_V will be in millilitres per cubic metre.

12 Interferences

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 minimized by proper selection of gas chromatographic columns and conditions and by stringent conditioning of both the sorbent tubes and analytical system before use.

This part of ISO 16017 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

NOTE 1 Suitable water elimination or reduction procedures include: sample splitting; 'dry purging' moisture from the secondary focusing trap and reducing the air volume sampled to 0,5 l.

shall be taken to prevent water interfering with the analytical process.

NOTE 2 A sorption tube which at first shows a good level of blank values may give rise to formation of artefacts later on. Ozone [11, 17] and nitrogen oxides in the presence of water [12] may damage Tenax TA. Benzaldehyde and acetophenone are possible products of these reactions. If Tenax TA does not show the necessary stability because of the presence of aggressive gases, Carbopack may be used as a sorbent [12, 13, 14].

As ozone and nitrogen oxides may react with the components to be measured, one must consider this by choosing sampling volumes as small as possible if gases of this kind are to be expected in larger amounts in the air sampled.

13 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 F and Tables 7 to 13.

14 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 and any supplementary standards;
- c) the sampling location, sampling time period and volume of air pumped;
- d) the barometric pressure and temperature, if required by clause 11;
- 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.

15 Quality control

An appropriate level of quality control should be employed, see [5].

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

Blank levels of benzene, toluene and xylene have been determined [15] on unspiked, conditioned tubes as specified in 6.1 and 7, and transported to field sites (in one survey, world-wide), exposed (closed) alongside sample tubes for one month and then returned to the laboratory for analysis. Results of Chromosorb 106 and Carbograph TD-1 are given in Table 13. For both sorbents, recoveries were in the low nanogram range, slightly higher than indicated in [1] for freshly-conditioned Carbograph.

The safe sampling volumes of the sorbent tubes should be retested annually or once every twenty uses (whichever comes first), using one of the procedures described in annex A or B. If the safe sampling volumes of the tube fall below the normal air sample collection volume for the analytes in question, the tube should be repacked with fresh sorbent and reconditioned.

Table 1 — Extrapolated retention volumes and safe sampling volumes (SSV) for organic vapours sampled on a 300 mg Chromosorb 106 sorbent tube at 20 °C

Organic compound	Boiling point °C	Vapour pressure kPa (25 °C)	Retention volume l	SSV ^a l	SSV per gram l/g	Desorption temperature °C	Ref.
Hydrocarbons							
Propane ^b	42	—	0,17	0,09	0,29	—	[2]
Pentane	35	56	23	12	39	130	[2]
Hexane	69	16	74	37	120	160	[2]
Heptane	98	4,7	330	160	530	180	[1]
Octane	125	1,4	2 100	1 000	3 300	200	[1]
Nonane	151	—	14 000	7 000	2,3 · 10 ⁴	220	[1]
Decane	174	—	6,2 · 10 ⁴	3,1 · 10 ⁴	1,0 · 10 ⁵	250	[2]
Benzene	80	10,1	57	28	95	160	[2]
Toluene	111	2,9	160	80	270	200	[1]

Table 2 — Extrapolated retention volumes and safe sampling volumes (SSV) for organic vapours sampled on a 500 mg Carboxen 569 sorbent tube at 20 °C [2]

Organic compound	Boiling point °C	Vapour pressure kPa (25 °C)	Retention volume l	SSV ^a l	SSV per gram l/g	Desorption temperature °C
Propane	42	—	7,2	3,6	7,2	200
Methanol ^b	65	12,3	4	2	4	200
Ethylene oxide	11	147	140	70	140	250
^a See clause 9, notes 1 and 2. ^b Desorption recovery is poor (see Table 7).						

Table 3 — Extrapolated retention volumes and safe sampling volumes for organic vapours sampled on a 200 mg Tenax TA sorbent tube at 20 °C [1]

Organic compound	Boiling point °C	Vapour pressure kPa (25 °C)	Retention volume l	SSV ^a l	SSV per gram l/g	Desorption temperature °C
Hydrocarbons						
Hexane	69	16	6,4	3,2	16	110
Heptane	98	4,7	34	17	85	130
Octane	125	1,4	160	80	390	140
Nonane	151	—	1 400	700	3 500	150
Decane	174	—	4 200	2 100	1,0 · 10 ⁴	160
Undecane	196	—	2,5 · 10 ⁴	1,2 · 10 ⁴	6,0 · 10 ⁴	170
Dodecane	216	—	1,26 · 10 ⁵	6,3 · 10 ⁴	3,0 · 10 ⁵	180
Benzene	80	10,1	13	6,2	31	120
Toluene	111	2,9	76	38	90	140
Xylene	138 to 144	0,67 to 0,87	600	300	1 500	140
Ethylbenzene	136	0,93	360	180	900	145
Propylbenzene	159	—	1 700	850	4 000	160
Isopropylbenzene	152	—	960	480	2 400	160
Ethyltoluene	162	—	2 000	1 000	5 000	160
Trimethylbenzene	165 to 176	—	3 600	1 800	8 900	170
Styrene	145	0,88	600	300	1 500	160
Methylstyrene	167	—	2 400	1 200	6 000	170
Chlorinated hydrocarbons						
Carbon tetrachloride	76	12	12	6,2	31	120
1,2-Dichloroethane	84	8,4	11	5,4	27	120
1,1,1-Trichloroethane	74	2,7	not recommended on Tenax			
1,1,2-Trichloroethylene	114	—	68	34	170	120
1,1,1,2-Tetrachloroethane	130	—	160	78	390	150
1,1,2,2-Tetrachloroethane	146	0,67	340	170	850	150
Trichloroethylene	87	2,7	11,2	5,6	28	120
Tetrachloroethylene	121	1,87	96	48	240	150
Chlorobenzene	131	1,2	52	26	130	140

Organic compound	Boiling point °C	Vapour pressure kPa (25 °C)	Retention volume l	SSV ^a l	SSV per gram l/g	Desorption temperature °C
Esters and glycol ethers						
Ethyl acetate	71	9,7	7,2	3,6	18	120
Propyl acetate	102	3,3	36	18	92	140
Isopropyl acetate	90	6,3	12	6	31	120
Butyl acetate	126	1,0	170	85	420	150
Isobutyl acetate	115	1,9	265	130	650	130
<i>t</i> -Butyl acetate	98	—	not recommended on Tenax			
Methyl acrylate	81	—	13	6,5	32	120
Ethyl acrylate	100	3,9	48	24	120	120
Methyl methacrylate	100	3,7	55	27	130	120
Methoxyethanol	125	0,8	6	3	15	120
Ethoxyethanol	136	0,51	10	5	25	130
Butoxyethanol	170	0,1	70	35	170	140
Methoxypropanol	118	—	27	13	65	115
Methoxyethyl acetate	145	0,27	16	8	40	120
Ethoxyethyl acetate	156	0,16	30	15	75	140
Butoxyethyl acetate	192	0,04	300	150	750	160
Aldehydes and ketones						
Methyl ethyl ketone	80	10,3	6,4	3,2	16	120
Methyl isobutyl ketone	118	0,8	52	26	130	140
Cyclohexanone	155	0,45	340	170	850	150
3,5,5-Trimethylcyclohex-2-enone	214	0,05	11 000	5 600	28 000	90
Furfural	162	0,5	600	300	1 500	200
Alcohols						
<i>n</i> -Butanol	118	0,67	10	5	25	120
Isobutanol	108	1,6	5,6	2,8	14	120
<i>t</i> -Butanol	83	1,17	not recommended on Tenax			
Octanol	180	—	2 800	1 400	7 000	160
Phenol	182	0,03	480	240	1 200	190
Others						
Maleic anhydride	202	6.E-6	180	88	440	180
Pyridine	116	16	8	40	150	—
Aniline	184	0,09	440	220	1 100	190
Nitrobenzene	211	0,02	28 000	14 000	70 000	200

^a See clause 9, notes 1 and 2.

Table 6 — Extrapolated retention volumes and safe sampling volumes (SSV) for organic vapours sampled on a 300 mg charcoal sorbent tube at 20 °C [1]

Organic compound	Boiling point °C	Vapour pressure kPa (25 °C)	Retention volume l	SSV ^a l	SSV per gram l/g	Desorption temperature °C
Propane	−42	—	10 ^b	5	15	220 ^b
Butane	−0,5	—	900 ^b	450	600	270 ^b
Pentane	35	56	2,7 · 10 ⁴	1,3 · 10 ⁴	4,3 · 10 ⁴	327
Hexane	69	16	1,5 · 10 ⁶	7,5 · 10 ⁵	2,5 · 10 ⁶	388
Benzene	80	10,1	3,4 · 10 ⁵	1,7 · 10 ⁵	5,6 · 10 ⁵	370

^a See clause 9, notes 1 and 2. Reduce SSV by a factor of 10 if sampling at high humidity; reduce SSV by a factor of 2 if sampling at high concentration.

^b Extrapolated from data on pentane, hexane and benzene.

Table 7 — Precision of analysis and storage of test compounds on Chromosorb 106 and Carboxen 569 [2] (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	
a-Pinene	4,2; 2,5		104	
Decane	4,2		104	
Propylene oxide	3,6		103	
Hexanal	3,5		98	

Organic compound	Loading µg	Times = 0 % CV ^a	Times = 5 months mean recovery ^b + % CV		Times = 11 months mean recovery + % CV	
			Recovery	Precision	Recovery	Precision
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						
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
^a Six replicates. ^b Normalized to toluene = 100. The stability of toluene has been established in a BCR intercomparison [7].						

Table 9 — Precision (repeatability and reproducibility) on Chromosorb 106

Loading level µg	Recovery %	ISO repeatability %	ISO reproducibility %
0,5	95,4	21,6	39,1
2,5	91,5	11,2	43,2
12,5	97,6	7,2	43,0
50	102,3	11,9	25,9

250	Overall	104,5	9,7			31,6		
		98,3	12,3			36,6		
Table 10	— Recovery (%) of benzene, toluene and xylene from spiked tubes							
Study No.			(%) Recovery					
		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	
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	

NOTE
200 ng.

In study 1, the spiked amounts of each hydrocarbon were approximately 80 ng; in studies 2 and 3, the masses were approximately

Table 11 — Standard deviation of the complete procedure — Application example 1

Substance	Mass concentration $\mu\text{g}/\text{m}^3$	Standard deviation %	Number of measurements	Mass concentration $\mu\text{g}/\text{m}^3$	Standard deviation %	Number of measurements
Isopentane	190	6,3	9	15,1	14,4	12
<i>n</i> -Pentane	148	6,8	10	11,9	15,3	11
Benzene	162	7,4	10	13,7	16,0	11
Toluene	189	8,2	10	15,6	16,5	12

Table 12 — Standard deviation of the complete procedure

Substance	Mass concentration $\mu\text{g}/\text{m}^3$	Standard deviation $\mu\text{g}/\text{m}^3$
<i>n</i> -Hexane	110	5,6 = 5 %
<i>n</i> -Heptane	19,1	0,5 = 3 %
Benzene	31	2,7 = 9 %
Toluene	66	1,9 = 3 %
<i>m</i> -Xylene	16,8	0,9 = 5 %

Table 13 — Blank levels for benzene, toluene and xylene for Chromosorb 106 and Carbograph TD-1													
Study No.		Chromosorb 106						Carbograph TD-1					
		Benzene		Toluene		Xylene		Benzene		Toluene		Xylene	
		$\mu\text{g}/\text{m}^3$	ng	$\mu\text{g}/\text{m}^3$	ng	$\mu\text{g}/\text{m}^3$	ng	$\mu\text{g}/\text{m}^3$	ng	$\mu\text{g}/\text{m}^3$	ng	$\mu\text{g}/\text{m}^3$	ng
1. UK survey	Mean	0,39	7,69	0,06	1,39	0,16	3,23	0,27	7,22	0,08	2,04	0,26	5,59
	Standard deviation (\pm)	0,12	1,96	0,03	0,55	0,09	1,64	0,11	2,75	0,03	0,78	0,12	2,28
	<i>n</i>	20		20		20		18		19		19	
2. VOC air comparison	Mean	0,58	10,38	0,15	3,26	0,08	1,46	0,28	6,88	0,15	3,34	0,12	2,35
	Standard deviation (\pm)	0,13	2,28	0,11	2,55	0,08	1,44	0,13	2,70	0,07	1,3	0,08	1,39
	<i>n</i>	14		14		14		14		14		14	
3. World survey	Mean	0,25	5,63	0,09	2,09	0,04	0,96	0,12	2,61	0,2	4,39	0,07	1,63
	Standard deviation (\pm)	0,14	3,04	0,11	2,36	0,02	0,51	0,05	1,13	0,28	6,19	0,05	1,17
	<i>n</i>	16		16		16		16		16		16	

Annex A

(normative)

Determination of breakthrough volumes from gas standards

A.1 Apparatus

Ordinary laboratory apparatus and

A.1.1 Sorbent tube, as described in 6.1.

A.1.2 Flow meter, with range 20 ml/min to 200 ml/min, traceably calibrated to a primary flow standard.

A.1.3 Flame ionization detector or similar.

A.2 Reagents

A.2.1 Dynamic standard concentration of organic vapour in air.

This standard atmosphere may be prepared by dilution of a measured amount of organic vapour with a metered flow of air. Examples of methods of generating standard atmospheres are given in 5.5.

A.3 Determination

A.3.1 Assemble a gas train consisting of a dynamic standard atmosphere generator delivering a concentration equivalent to a current exposure limit for the analyte of interest, a sorbent tube, a flowmeter and a flame ionization detector. Pass the gas through the train at a known flowrate between 20 ml/min and 200 ml/min. Use a value in this range appropriate for the sampling rate intended. Note the time that the flow was initiated. When the vapour begins to emerge, the detector will show a response. Continue the measurement until a plateau corresponding to the input is reached. Determine the time at which 5 % of the input value is reached.

A.3.2 If the dead volume of the system is significant in comparison with the breakthrough volume, determine the dead volume by repeating the determination with an empty tube in the gas train and make a suitable correction.

A.3.3 Determine the effect of moisture on the breakthrough volume by humidifying the gas stream to approximately 80 % RH. Do this by diluting a primary gas stream with air at 100 % RH obtained by passing air through a series of water bubblers. Do not pass the organic vapour atmosphere through the water.

A.4 Expression of results

Calculate the breakthrough volume by multiplying the flowrate, expressed in litres per minute, by the elapsed time in minutes, taking the time elapsed from the point of flow initiation to the point where 5 % of the plateau value was reached.

Annex B (normative)

Determination of breakthrough volume from the extrapolated retention volume

B.1 Apparatus

Ordinary laboratory apparatus and

B.1.1 Sorbent tubes, as defined in 6.1.

B.1.2 Gas chromatograph, fitted with a flame ionization detector, capable of detecting an injection of 0,5 ng toluene with a signal-to-noise ratio of at least 5 to 1.

B.1.3 Flow meter, with a range of 20 ml/min to 200 ml/min.

B.1.4 Thermocouple.

B.2 Reagents

B.2.1 Dynamic standard concentration of organic vapour in air.

This standard atmosphere may be prepared by dilution of a measured amount of organic vapour with a metered flow of air. Examples of methods of generating standard atmospheres are given in 5.5.

B.3 Determination

Connect a sorbent tube (B.1.1) to the injection and detection ports of a gas chromatograph (B.1.2) in place of the normal chromatography column by means of narrow bore PTFE tubing. Determine the retention volume of a 1-ml aliquot of standard atmosphere (B.2.1; approximately 300 mg/m³ at 20 °C) at least five settings of the chromatograph oven temperature such that the retention time is convenient (between 2 min and 20 min). Calculate the retention volume by multiplying the retention time by the column volumetric flowrate. Repeat the determination five times at each temperature.

B.4 Expression of results

Plot the mean values of the determinations of retention volume at each temperature against reciprocal absolute temperature and extrapolate to 20 °C.

Annex C (informative)

Description of sorbent types

Sorbent	Type
Carbotrap	Graphitized carbon
Carbopack	Graphitized carbon
Carbograph TD-1	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
Porapak N	Vinylpyrrolidone
Porapak Q	Ethylvinylbenzene/divinylbenzene
Spherocarb	Carbon molecular sieve
Tenax TA	Poly(diphenyl oxide)
Tenax GR	Graphitized poly(diphenyl oxide)

NOTE Carbotrap™, Carbopack™, Carbograph TD-1™, Carbosieve SIII™ and Carboxen™ are trademarks of Supelco, Inc., USA; Tenax™ is a trademark of Enka Research Institute, NV, NL; Chromosorb™ is a trademark of Manville Corp, USA; Porapak™ is a trademark of Waters Associates Inc., USA; Spherocarb™ is a trademark of Analabs Inc., 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 product named. Equivalent products may be used if they can be shown to lead to the same results.

Annex D (informative)

Guidance on sorbent selection

Sample tube sorbent	Approx. analyte volatility range	Max. temp. °C	Specific surface area m ² /g	Analyte examples
Carbotrapä C Carbopackä C	n-C ₈ to n-C ₂₀	> 400	12	Alkylbenzenes and aliphatics ranging in volatility from n-C ₈ to n-C ₁₆ .
Tenaxä TA	boiling point 100 °C to 400 °C n-C ₆ to n-C ₂₆	350	35	Aromatics, non-polar components (boiling point > 100 °C) and less volatile polar components (boiling point > 150 °C).
Tenax GR	boiling point 100 °C to 450 °C n-C ₇ to n-C ₃₀	350	35	Alkylbenzenes, vapour phase PAHs & PCBs and as above for Tenax TA.
Carbotrap Carbopack B Carbograph TD-1	(n-C ₄) n-C ₅ to n-C ₁₄	> 400	100	Wide range of VOCs, including ketones, alcohols, and aldehydes (boiling point > 75 °C) and all non-polar compounds within the volatility range specified. Plus perfluorocarbon tracer gases.
Chromosorbä 102	boiling point 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	boiling point 50 °C to 200 °C	250	750	Suits a wide range of VOCs, including hydrocarbons from n-C ₅ to n-C ₁₂ . Also good for volatile oxygenated compounds.
Porapakä Q	boiling point 50 °C to 200 °C n-C ₅ to n-C ₁₂	250	550	Suits a wide range of VOCs, including oxygenated compounds.
Porapak N	boiling point 50 °C to 150 °C n-C ₅ to n-C ₈	180	300	Specifically selected for volatile nitriles; acrylonitrile, acetonitrile and propionitrile. Also good for pyridine, volatile alcohols from EtOH, MEK, etc.
Spherocarbä ^a	-30 °C to 150 °C C ₃ to n-C ₈	> 400	1 200	Good for very volatile compounds such as VCM, ethylene oxide, CS ₂ and CH ₂ Cl ₂ . Also good for volatile polars, e.g. MeOH, EtOH and acetone.
Carbosieveä S-III ^a or Carboxenä 1000 ^a	-60 °C to 80 °C	400	800	Good for ultra-volatile compounds such as C ₃ , C ₄ hydrocarbons, volatile haloforms and freons.
Molecular sieve ^b	-60 °C to 80 °C	350		Used specifically for 1,3-butadiene and nitrous oxide.
NOTE Trademark designations are given in annex C.				
^a These sorbents exhibit some water retention. Safe sampling volumes should be reduced by a factor of 10 if sampling a high (> 90%) relative humidity.				
^b Significantly hydrophilic. Do not use in high humidity atmospheres unless special precautions are taken.				

Annex E (informative)

Guidance on sorbent use

Sample tube sorbent	Maximum temp. °C	Hydrophobic	Temp. and gas flowrate for conditioning a	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 Carbopack B Carbograph TD-1	> 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 trap 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 trap 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 trap 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 trap or Porapak N
Spherocarb b	> 400	No	400 °C and 100 ml/min	390 °C and 30 ml/min	Dual-bed Carbopack B plus carbon molecular sieve trap or Spherocarb
Carbon molecular sieve such as Carbosieve S- III b or Carboxen 1000 b	400	No	350 °C and 100 ml/min	325 °C and 30 ml/min	Dual-bed Carbopack B plus carbon molecular sieve trap or carbon molecular sieve alone
Molecular sieve c	350	No	330 °C and 100 ml/min	300 °C and 30 ml/min	Dual-bed Carbopack B plus carbon molecular sieve trap 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 b 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 trap
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 C.					

a The conditioning temperature is not the same as the pre-conditioning temperature. (See 5.3).

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

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

Annex F (informative)

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

F.1 Data on overall uncertainty

Laboratory tests of the procedure [2], following in part EN 1076, using tubes as specified in 6.1 spiked from a standard atmosphere of hexane at 1,0 mg/m³ and 50 % R.H. at 20 °C and using a pump in conformity with EN 1232 [10], yielded results expressed as overall uncertainty (EN 482) [9]: Tenax TA, Tenax GR and Chromosorb 106 (mean of five determinations), 8,9 %; Carbopack B and Carbotrap (mean of three determinations), 16,8 %.

F.2 Data on precision and bias

Most tests of the performance of this procedure have examined only analytical precision. A summary of existing data on laboratory tests using tubes as specified in 6.1 is presented. To determine overall uncertainty, it is necessary also to know the sampling (pump) error and the bias. However, the reproducibility data enable an estimate to be made of the between-laboratory variance, which is not available from the overall uncertainty values in F.1.

Laboratory tests [2] on tubes liquid spiked with the compounds specified in 5.1 on Chromosorb 106 or Carboxen 569 at a load level of approximately 1,0 µg are summarized in Table 7. The precision, expressed as a coefficient of variation, was between 1,3 % and 5,9 %, depending on analyte. Expressed as repeatability (ISO 5725-1) the range is equivalent to 3,7 % to 16,7 %.

Laboratory tests [1] on tubes liquid spiked with a broader range of compounds on Tenax TA at a single load level of approximately 10 µg are summarized in Table 8. The precision expressed as a coefficient of variation, was between 0,4 % and 2,8 %, depending on analyte. Expressed as repeatability (ISO 5725-1) the range is equivalent to 1,1 % to 5,6 %.

Laboratory tests [6] on tubes vapour spiked with 11 model compounds including benzene, toluene, xylene and isopropylbenzene on Chromosorb 106 at load levels between 0,5 mg and 250 µg are summarized in Table 9. The precision, expressed as repeatability (ISO 5725-1) was between 7,2 % and 21,6 %, depending on loading level. The precision, expressed as reproducibility (ISO 5725-1) was between 25,9 % and 43,2 %, depending on loading level.

Laboratory tests [15] on tubes liquid spiked with benzene, toluene and xylene at 80 ng or 200 ng levels are summarized in Table 10. Tubes were transported to field sites (in one survey, worldwide), exposed (closed) alongside sample tubes for 1 month and then returned to the laboratory for analysis. Recoveries for Chromosorb 106 and Carbograph TD-1 tubes were between 82,7 % and 105,9 %. The precision, expressed as a coefficient of variation, was between 3,2 % and 12,1 % depending on sorbent and analyte.

Laboratory tests [16] on tubes spiked from a standard atmosphere containing methane, ethane, propene, vinyl chloride, isobutane, isobutene, n-butane, isopentane, n-pentane, benzene and toluene at two different concentrations are summarized in Table 11. In this case, tubes were constructed of glass tubing, 6 mm OD, 4 mm ID and 150 mm long, containing a 63 mg bed of 35/60 mesh Tenax TA (nearest the sampling inlet) and a 297 mg bed of 35/60 mesh XAD-4. For the compounds listed in Table 11, the precision, expressed as a coefficient of variation was between 6,3 % and 8,2 % at the higher level and between 14,4 % and 16,5 % at the lower level. The remaining compounds were not quantitatively retained.

Laboratory tests [16] on tubes spiked from a standard atmosphere containing n-hexane, n-heptane, benzene, toluene and m-xylene are summarized in Table 12. In this case tubes were constructed of glass tubing, 8 mm OD, 5 mm ID and 260 mm long, adapted to 6,3 mm OD at each end, containing a 500 mg bed of Tenax TA (nearest the

sampling inlet) and a 300 mg bed of Carbosieve-S (60-80 mesh). The precision, expressed as a coefficient of variation, was between 3 % and 9 %, depending on analyte.

NOTE For workplace measurements, the laboratory test [2] on hexane at 1,0 mg/m³ demonstrate that for all sorbents tested, the procedure meets the requirements of EN 482, i.e. the overall uncertainty is better than 30 %. EN 482 allows a partial evaluation, where not all the tests in EN 1076 have been undertaken, to be counted as a full evaluation on a temporary basis. Laboratory tests [6] demonstrate that the precision of analysis does not vary significantly for all the compounds tested. It may be concluded that for the compounds in Tables 7 and 8 the procedure meets the requirements of EN 482; for additional compounds in Tables 1 to 6, only safe sampling volume data are available. For ambient and indoor air measurements, there is no equivalent to EN 1076. However, the laboratory tests [16,17] suggest that the precision of analysis of typical compounds is about three times the values obtained for workplace concentrations, the overall uncertainty, therefore, would be expected to be better than 50 %.

F.3 Data on storage

A summary of existing data on laboratory storage tests using tubes as specified in 6.1 is presented in Tables 7 and 8.

Laboratory tests [2] on tubes spiked with the 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 7. The mean recovery (relative to unstored tubes) for Chromosorb 106 was 105,6 %.

Laboratory tests [1] 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 8. Excluding hexane and methoxyethanol, the mean recovery (relative to unstored tubes) was 99,7 % and the mean coefficient of variation (s_{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 CRM 112 [7], the stability of a batch of tubes charge 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 40 °C, recoveries were respectively 102 % to 104 % and 100 % to 104 %. No instability was detected after 25 months, but recoveries were not reported.

Storage stability data of sub-microgram amounts of the EPA TO-14 mix of non-polar VOCs on two types of single-bed and three types of multi-bed carbon thermal desorption tubes have been published [15]. Recoveries after storage at 4 °C or 20 °C for up to 21 weeks are very dependent on both the sorbent(s) used and the compound, and the original data should be consulted. There was some evidence of dehydrochlorination of certain compounds, notably 1,1,2,2-tetrachloroethane, which may be a function of desorption conditions rather than storage time.

NOTE 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 may help to reduce any cross-reaction of sorbed VOCs.

Bibliography

- [1] UK Health and Safety Executive. *Methods for the Determination of Hazardous Substances*. Volatile organic compounds in air — Laboratory method using pumped solid sorbent tubes, thermal desorption and gas chromatography. MDHS 72. HSE: (1992) London.
- [2] *Study of sorbing agents for the sampling of volatile compounds from air*. EC Contract MAT1-CT92-0038. Final Report (1995).
- [3] STERNBERG, J. C. The mechanism of response of flame ionization detectors. *Proc. 3rd Intern. Symp. Gas Chromatog.* (1960) pp. 231-267.
- [4] BROWN, R. H. and PURNELLI, C. J. Collection and Analysis of Trace Organic Vapour Pollutants in Ambient Atmospheres. The Performance of Tenax-GC Adsorbent Tube. *J. Chromatog.*, **178**, (1979) pp. 79-90.
- [5] UK Health and Safety Executive. *Methods for the Determination of Hazardous Substances*. Analytical quality in workplace air monitoring. MDHS 71. HSE: (1991) London.
- [6] COKER, D. T. *et al.* A monitoring method for gasoline vapour giving detailed composition. *Ann. Occup. Hyg.* **33**, (1989) pp. 15-26.
- [7] VANDENDRIESSCHE, S. *et al.* Certification of a Reference Material for Aromatic Hydrocarbons in Tenax Samplers. *Analyst*, **116**, (1991) pp. 437-441.
- [8] UK Health and Safety Executive. *Methods for the Determination of Hazardous Substances*. Generation of standard atmospheres — Syringe injection method MDHS 3. HSE: (1983) London.
- [9] EN 482:1994, Workplace atmospheres — General requirements for performance of procedures for the measurement of chemical agents.
- [10] EN 1232:1993, *Workplace atmospheres — Pumps for personal sampling of chemical agents-Requirements and test methods*.
- [11] KNOEPEL, H., VERSINO, B., SCHLITT, H., PEIL, A., SCHAUENBURG, H., VISSERS, H. Organics in air. Sampling and identification. *Proc. First European Symposium on physico-chemical behaviour of atmospheric pollutants*. ISPRA, 16-17 October 1979, pp. 25-40, Commission of the European Communities, Brussels-Luxemb. 1980.
- [12] DULSON, W. Organisch-chemische Fremdstoffe in atmosphärischer Luft. In: *Schriftenreihe des Vereins für Wasser-, Boden- und Lufthygiene*, **47**. Stuttgart: Gustav-Fischer-Verlag 1978.
- [13] BERTONI, G., BRUNER, F., LIBERTI, A., PERRINO, C. Some critical parameters in collection, recovery and chromatographic analysis of organic pollutants in ambient air using light adsorbents. *J. Chromatog.*, **203**, (1981), pp. 263-270.
- [14] VIDAL-MADJAR, C., GONNORD, M.-F., BENCHAH, F., GUICHON, G. Performances of various adsorbents for the trapping and analysis of organohalogenated air pollutants by gas chromatography. *J. Chromatog. Sci.*, **16** (1978), pp. 190-196.
- [15] WRIGHT, M.D., PLANT, M.T., BROWN, R.H., DE GRAFF, I.D. *Proc. Air and Waste Management Assoc. Conf. on Measurement and Toxic and Related Air Pollutants*, VIP-85, September 1-3, 1998, Cary, North Carolina, USA. ISBN 0-923204-15-6.
- [16] VDI 3482-6, *Measurement of gaseous emissions: gas-chromatographic determination of organic compounds — Sampling by enrichment; thermal desorption*.

BSI — British Standards Institution

BSI is the independent national body responsible for preparing British Standards. It presents the UK view on standards in Europe and at the international level. It is incorporated by Royal Charter.

Revisions

British Standards are updated by amendment or revision. Users of British Standards should make sure that they possess the latest amendments or editions.

It is the constant aim of BSI to improve the quality of our products and services. We would be grateful if anyone finding an inaccuracy or ambiguity while using this British Standard would inform the Secretary of the technical committee responsible, the identity of which can be found on the inside front cover. Tel: 020 8996 9000. Fax: 020 8996 7400.

BSI offers members an individual updating service called PLUS which ensures that subscribers automatically receive the latest editions of standards.

Buying standards

Orders for all BSI, international and foreign standards publications should be addressed to Customer Services. Tel: 020 8996 9001. Fax: 020 8996 7001. Standards are also available from the BSI website at <http://www.bsi-global.com>.

In response to orders for international standards, it is BSI policy to supply the BSI implementation of those that have been published as British Standards, unless otherwise requested.

Information on standards

BSI provides a wide range of information on national, European and international standards through its Library and its Technical Help to Exporters Service. Various BSI electronic information services are also available which give details on all its products and services. Contact the Information Centre. Tel: 020 8996 7111. Fax: 020 8996 7048.

Subscribing members of BSI are kept up to date with standards developments and receive substantial discounts on the purchase price of standards. For details of these and other benefits contact Membership Administration. Tel: 020 8996 7002. Fax: 020 8996 7001. Further information about BSI is available on the BSI website at <http://www.bsi-global.com>.

Copyright

Copyright subsists in all BSI publications. BSI also holds the copyright, in the UK, of the publications of the international standardization bodies. Except as permitted under the Copyright, Designs and Patents Act 1988 no extract may be reproduced, stored in a retrieval system or transmitted in any form or by any means – electronic, photocopying, recording or otherwise – without prior written

of necessary details such as symbols, and size, type or grade designations. If these permission from BSI.

This does not preclude the free use, in the course of implementing the standard, details are to be used for any other purpose than implementation then the prior written permission of BSI must be obtained.

If permission is granted, the terms may include royalty payments or a licensing agreement. Details and advice can be obtained from the Copyright Manager. Tel: 020 8996 7070.

