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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 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)

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Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 734 10 79
E-mail copyright@iso.ch
Web www.iso.ch

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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 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*:

- *Part 1: Pumped sampling*
- *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.

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

Part 1:
Pumped 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 ambient, indoor and workplace atmospheres and the assessment of emissions from materials in small- or full-scale test chambers.

This part of ISO 16017 is appropriate for a wide range of VOCs, including hydrocarbons, halogenated hydrocarbons, esters, glycol ethers, ketones and alcohols. A number of sorbents [1] are recommended for the sampling of these VOCs, each sorbent having a different range of applicability. Very polar compounds will generally require derivatization, very low boiling compounds will only be partially retained by the sorbents, depending on ambient temperature, and can only be estimated qualitatively. Semi-volatile compounds will be fully retained by the sorbents, but may only be partially recovered. Compounds for which this part of ISO 16017 has been tested are given in tables. This part of ISO 16017 may be applicable to compounds not listed, but in these cases it is advisable to use a back-up tube containing the same or a stronger sorbent.

This part of ISO 16017 is applicable to the measurement of airborne vapours of VOCs in a concentration range of approximately 0,5 μg/ m^3 to 100 mg/m^3 individual compound.

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 sorptive capacity is measured as a breakthrough volume of air, which determines the maximum air volume that shall not be exceeded when sampling.

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 and molecular sieves such as Spherocarb, or pure charcoal; at low nanogram levels for Tenax TA and at 5 ng to 50 ng levels for other porous polymers such as Chromosorbs and Porapaks. Sensitivity is typically limited to 0,5 μg/m^3 for 10-litre air samples with this latter group of sorbents because of their inherent high background.

The procedure specified in this part of ISO 16017 is applicable to low flowrate personal sampling pumps and gives a time-weighted average result. It is not applicable to the measurement of instantaneous or short-term fluctuations in concentration.

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[1] The sorbents listed in annex C and elsewhere in this International Standard 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.

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

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[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/m^3 and 100 µg/m^3. 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^3 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^3 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 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 (5.2), stopper and shake to mix.

5.7.4 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 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 °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 µl 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 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 × 0,22 mm fused silica columns with thick-film (1 µm to 5 µm) 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):

$$c_{\mathrm{m}} = \frac{m_{\mathrm{F}} - m_{\mathrm{B}}}{V} \cdot 1\,000 \qquad (1)$$

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:

$$c_{\mathrm{c}} = c_{\mathrm{m}} \cdot \frac{101}{p} \cdot \frac{T + 273}{298} \qquad (2)$$

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:

$$c_V = c_m \cdot \frac{24{,}5}{M} \cdot \frac{101}{p} \cdot \frac{T + 273}{298} \tag{3}$$

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

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.

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	$2,3 \times 10^4$	220	[1]
Decane	174	—	$6,2 \times 10^4$	$3,1 \times 10^4$	$1,0 \times 10^5$	250	[2]
Benzene	80	10,1	57	28	95	160	[2]
Toluene	111	2,9	160	80	270	200	[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	Ref.
Xylene	138 to 144	0,67 to 0,87	1 600	770	2 600	250	[1]
Ethylbenzene	136	0,93	730	360	1 200	250	[1]
Trimethylbenzene	165 to 176	—	5 600	2 800	9 300	250	[1]
α-Pinene [c]	53	0,51	6 600	3 300	$1,1 \times 10^4$	200	[2]
Chlorinated hydrocarbons							
Dichloromethane	40	47	6,9	3,5	12	130	[2]
Carbon tetrachloride	76	12	44	22	73	160	[1]
1,2-Dichloroethane	84	8,4	34	17	67	150	[1]
Trichloroethylene	—	2,7	80	40	140	170	[1]
1,1,1-Thrichloroethane	74	13,3	43	22	71	140	[2]
Esters and glycol ethers							
Methyl acetate	58	22,8	14	7	23	125	[2]
Ethyl acetate	71	9,7	39	20	67	150	[1]
Propyl acetate	102	3,3	300	150	500	170	[1]
Isopropyl acetate	90	6,3	150	75	250	165	[1]
Butyl acetate	126	1,0	1 500	730	2 400	95	[1]
Isobutyl acetate	115	1,9	880	440	1 500	90	[1]
t-Butyl acetate	98	—	330	160	530	185	[1]
Methoxyethanol	125	0,8	45	23	75	140	[2]
Ethoxyethanol	136	0,51	150	75	200	250	[1]
Methoxyethyl acetate	145	0,27	1 700	860	2 900	250	[1]
Ethoxyethyl acetate	156	0,16	8 100	4 000	$1,3 \times 10^4$	250	[1]
Ketones							
Acetone	56	24,6	2,9	1,5	5	120	[1]
Methyl ethyl ketone	80	10,3	21	11	35	145	[2]
Methyl isobutyl ketone	118	0,8	490	250	830	190	[1]
Alcohols							
Methanol [b]	65	12,3	0,78	0,39	1,3	—	[2]
Ethanol	78	5,9	3,2	1,6	5,3	120	[2]
n-Propanol	97	1,9	17	8	27	125	[1]
Isopropanol	82	4,3	88	44	15	120	[1]
n-Butanol	118	0,67	140	68	230	170	[2]
Isobutanol	108	1,6	60	30	100	150	[1]
Others							
Ethylene oxide [b]	11	147	0,84	0,42	1,4	100	[2]
Propylene oxide	34	59	2,0	1,0	3,4	120	[2]
Hexanal	131	—	1 680	840	2 800	220	[2]

[a] See clause 9, notes 1 and 2.

[b] SSV below recommended 1 l, Carboxen 569 is preferred (Table 2).

[c] α-pinene is anomalous on Tenax but apparently normal on Chromosorb 106.

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	$1,0 \times 10^4$	160
Undecane	196	—	$2,5 \times 10^4$	$1,2 \times 10^4$	$6,0 \times 10^4$	170
Dodecane	216	—	$1,26 \times 10^5$	$6,3 \times 10^4$	$3,0 \times 10^5$	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
t-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						
n-Butanol	118	0,67	10	5	25	120
Isobutanol	108	1,6	5,6	2,8	14	120
t-Butanol	83	1,17	not recommended on Tenax			
Octanol	180	—	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 4 — Extrapolated retention volumes and safe sampling volumes for organic vapours sampled on a 500 mg Porapak N 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						
Pentane	35	56	8,2	4,1	8,2	180
Hexane	69	16	32	16	32	180
Heptane	98	4,7	190	95	190	180
Benzene	80	10	52	26	52	180
Alcohols						
Ethanol	78	5,9	7,5	3,7	7,5	120
n-Propanol	97	1,9	40	20	40	120
n-Butanol	118	0,67	10	5	25	120
Isobutanol	108	1,6	5,6	2,8	14	120
Octanol	180	—	2 800	1 400	7 000	160
Phenol	182	0,03	480	240	1 200	190
Others						
Acetic acid	116	—	97	50	97	180
Acetonitrile	82	9,9	7	3,5	7	180
Acrylonitrile	77	13,3	16	8	16	180
Propionitrile	97	—	23	11	23	180
Pyridine	116	—	390	200	390	180
Methyl ethyl ketone	80	10,3	95	50	95	180

[a] See clause 9, notes 1 and 2. Reduce SSV by factor of 2 if sampling at high humidity.

Table 5 — Extrapolated retention volumes and safe sampling volumes (SSV) for organic vapours sampled on a 300 mg Spherocarb 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
Butane	–0,5	—	1 600	820	2 700	270
Pentane	35	56	$6,3 \times 10^4$	$3,0 \times 10^4$	$1,0 \times 10^5$	335
Hexane	69	16	$3,9 \times 10^6$	$2,0 \times 10^6$	$7,0 \times 10^6$	390
Benzene	80	10,1	$1,0 \times 10^6$	$5,0 \times 10^5$	$1,7 \times 10^6$	375
Dichloromethane	40	47	400	200	700	250
1,1,1-Trichloroethane	74	13,3	$1,8 \times 10^4$	$9,0 \times 10^3$	$2,7 \times 10^4$	290
Methanol	65	12,3	1260	130	430	340
Ethanol	78	5,9	6 900	3 500	$1,2 \times 10^3$	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.

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	$2{,}7 \times 10^4$	$1{,}3 \times 10^4$	$4{,}3 \times 10^4$	327
Hexane	69	16	$1{,}5 \times 10^6$	$7{,}5 \times 10^5$	$2{,}5 \times 10^6$	388
Benzene	80	10,1	$3{,}4 \times 10^5$	$1{,}7 \times 10^5$	$5{,}6 \times 10^5$	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	
α-Pinene	4,2; 2,5		104	
Decane	4,2		104	
Propylene oxide	3,6		103	
Hexanal	3,5		98	

Table 8 — Precision and storage recovery of solvents on Tenax TA sorbent tubes

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**
Hydrocarbons						
Hexane	7,8	10,7	93,6	17,9	100,8	26,1
Heptane	8,4	2,4	99,5	2,1	100,0	1,3
Octane	8,6	2,4	100,1	1,8	100,0	0,5
Nonane	12,0	0,8	nd	nd	101,0	0,4
Decane	9,2	2,2	100,4	1,5	100,2	0,5
Undecane	9,1	2,3	100,7	1,5	100,2	0,2
Dodecane	9,9	2,8	101,8	1,5	101,5	0,4
Benzene	11,0	2,5	98,7	2,0	98,6	0,8
Toluene	10,9	2,6	(100,0)	1,8	(100,0)	0,6
p-Xylene	5,3	2,5	99,9	1,7	99,8	0,7
o-Xylene	11,0	2,4	100,0	1,7	98,8	0,7
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
m + *p*-Ethyltoluene	10,5	2,3	98,8	1,7	96,9	1,2
o-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
Esters and glycol ethers						
Ethyl acetate	10,3	0,6	97,6	1,0	100,0	2,5
Propyl acetate	10,9	2,4	100,5	1,7	99,1	0,8
Isopropyl acetate	9,4	1,0	97,0	0,4	100,0	1,4
Butyl acetate	10,8	2,4	100,3	1,6	99,9	0,6
Isobutyl acetate	10,7	2,3	100,2	1,4	99,8	0,7
Methoxyethanol	8,9	5,4	87,3	5,7	93,1	1,6
Ethoxyethanol	10,4	4,2	97,6	2,5	97,2	3,3
Butoxyethanol	10,0	2,6	100,6	4,1	100,1	3,0
Methoxypropanol	10,4	2,4	95,3	3,6	99,0	1,2
Methoxyethyl acetate	12,5	2,1	100,6	1,4	98,9	1,4
Ethoxyethyl acetate	11,4	0,9	99,8	2,2	98,7	2,6
Butoxyethyl acetate	11,5	2,3	101,3	1,3	99,9	1,1
Aldehydes and ketones						
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

Organic compound	Loading	Times = 0	Times = 5 months mean recovery [b] + % CV		Times = 11 months mean recovery + % CV	
	µg	% CV [a]	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	104,5	9,7	31,6
Overall	**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
	n	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
	n	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
	n	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
	n	3	3	3	3	3	3

NOTE In study 1, the spiked amounts of each hydrocarbon were approximately 80 ng; in studies 2 and 3, the masses were approximately 200 ng.

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

Substance	Mass concentration µg/m^3	Standard deviation %	Number of measurements	Mass concentration µg/m^3	Standard deviation %	Number of measurements
Isopentane	190	6,3	9	15,1	14,4	12
n-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 µg/m^3	Standard deviation µg/m^3
n-Hexane	110	5,6 = 5 %
n-Heptane	19,1	0,5 = 3 %
Benzene	31	2,7 = 9 %
Toluene	66	1,9 = 3 %
m-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	
		µg/m^3	ng	µg/m^3	ng	µg/m^3	ng	µg/m^3	ng	µg/m^3	ng	µg/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 (±)	0,12	1,96	0,03	0,55	0,09	1,64	0,11	2,75	0,03	0,78	0,12	2,28
	n	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 (±)	0,13	2,28	0,11	2,55	0,08	1,44	0,13	2,70	0,07	1,3	0,08	1,39
	n	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 (±)	0,14	3,04	0,11	2,36	0,02	0,51	0,05	1,13	0,28	6,19	0,05	1,17
	n	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/m^3 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^{TM}, Carbopack^{TM}, Carbograph TD-1^{TM}, Carbosieve SIII^{TM} and Carboxen^{TM} are trademarks of Supelco, Inc., USA; Tenax^{TM} is a trademark of Enka Research Institute, NV, NL; Chromosorb ^{TM} is a trademark of Manville Corp, USA; Porapak ^{TM} is a trademark of Waters Associates Inc., USA; Spherocarb ^{TM} 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.