INTERNATIONAL STANDARD

ISO 16000-6

Second edition
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Indoor air —

Part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA® sorbent, thermal desorption and gas chromatography using MS or MS-FID

Air intérieur —

Partie 6: Dosage des composés organiques volatils dans l'air intérieur des locaux et chambres d'essai par échantillonnage actif sur le sorbant Tenax TA®, désorption thermique et chromatographie en phase gazeuse utilisant MS ou MS-FID

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Foreword

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

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

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

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

ISO 16000-6 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 6, *Indoor air*.

This second edition cancels and replaces the first edition (ISO 16000-6:2004), which has been technically revised.

ISO 16000 consists of the following parts, under the general title *Indoor air*:

— *Part 1: General aspects of sampling strategy*

— *Part 2: Sampling strategy for formaldehyde*

— *Part 3: Determination of formaldehyde and other carbonyl compounds in indoor air and test chamber air — Active sampling method*

— *Part 4: Determination of formaldehyde — Diffusive sampling method*

— *Part 5: Sampling strategy for volatile organic compounds (VOCs)*

— *Part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA® sorbent, thermal desorption and gas chromatography using MS or MS-FID*

— *Part 7: Sampling strategy for determination of airborne asbestos fibre concentrations*

— *Part 8: Determination of local mean ages of air in buildings for characterizing ventilation conditions*

— *Part 9: Determination of the emission of volatile organic compounds from building products and furnishing — Emission test chamber method*

— *Part 10: Determination of the emission of volatile organic compounds from building products and furnishing — Emission test cell method*

— *Part 11: Determination of the emission of volatile organic compounds from building products and furnishing — Sampling, storage of samples and preparation of test specimens*

— *Part 12: Sampling strategy for polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polycyclic aromatic hydrocarbons (PAHs)*

— *Part 13: Determination of total (gas and particle-phase) polychlorinated dioxin-like biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDDs/PCDFs) — Collection on sorbent-backed filters*

— *Part 14: Determination of total (gas and particle-phase) polychlorinated dioxin-like biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDDs/PCDFs) — Extraction, clean-up and analysis by high-resolution gas chromatography and mass spectrometry*

— *Part 15: Sampling strategy for nitrogen dioxide (NO_2)*

— *Part 16: Detection and enumeration of moulds — Sampling by filtration*

— *Part 17: Detection and enumeration of moulds — Culture-based method*

— *Part 18: Detection and enumeration of moulds — Sampling by impaction*

— *Part 19: Sampling strategy for moulds*

— *Part 23: Performance test for evaluating the reduction of formaldehyde concentrations by sorptive building materials*

— *Part 24: Performance test for evaluating the reduction of volatile organic compound (except formaldehyde) concentrations by sorptive building materials*

— *Part 25: Determination of the emission of semi-volatile organic compounds by building products — Micro-chamber method*

— *Part 26: Sampling strategy for carbon dioxide (CO_2)*

— *Part 28: Determination of odour emissions from building products using test chambers*

The following parts are under preparation:

— *Part 21: Detection and enumeration of moulds — Sampling from materials*

— *Part 27: Determination of settled fibrous dust on surfaces by SEM (scanning electron microscopy) (direct method)*

— *Part 29: Test methods for VOC detectors*

— *Part 30: Sensory testing of indoor air*

— *Part 31: Measurement of flame retardants and plasticizers based on organophosphorus compounds — Phosphoric acid ester*

— *Part 32: Investigation of constructions on pollutants and other injurious factors — Inspections*

Introduction

ISO 16000-1 establishes general requirements relating to the measurement of indoor air pollutants and the important conditions to be observed before or during the sampling of individual pollutants or groups of pollutants. Aspects of the determination (sampling and analysis) and the sampling strategy of specific pollutants or groups of pollutants are specified in the subsequent parts of ISO 16000 (see Foreword).

ISO 16000-5 (dealing with VOC sampling strategy) is a link between ISO 16000-1 (a generic standard establishing the principles) and this part of ISO 16000, which deals with sampling and analytical measurements.

ISO 16017 (see Clause 2 and Reference [8]) and ISO 12219[3]–[7] also focus on volatile organic compound (VOC) measurements.

Indoor air —

Part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA® sorbent, thermal desorption and gas chromatography using MS or MS-FID

1 Scope

This part of ISO 16000 specifies a method for determination of volatile organic compounds (VOCs) in indoor air and in air sampled for the determination of the emission of VOCs from building products or materials and other products used in indoor environments using test chambers and test cells. The method uses Tenax TA®[1)] sorbent with subsequent thermal desorption (TD) and gas chromatographic (GC) analysis[13] employing a capillary column or columns and a flame ionization detector (FID) and/or a mass spectrometric (MS) detector.

The method is applicable to the measurement of non-polar and slightly polar VOCs at concentrations ranging from sub-micrograms per cubic metre to several milligrams per cubic metre. Using the principles specified in this method, some very volatile compounds (VVOC) and semi-volatile organic compounds (SVOC) can also be analysed (see Annex D).

2 Normative references

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

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

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

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
semi-volatile organic compound
SVOC
organic compound whose boiling point is in the range from (240 °C to 260 °C) to (380 °C to 400 °C)

NOTE 1 This classification has been defined by the World Health Organization[14].

1) Tenax TA® is the trade name of a product supplied by Buchem. This information is given for the convenience of users of this document 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.

NOTE 2 Boiling points of some compounds are difficult or impossible to determine because they decompose before they boil at atmospheric pressure. Vapour pressure is another criterion for classification of compound volatility that may be used for classification of organic chemicals[15].

3.2
volatile organic compound
VOC
organic compound whose boiling point is in the range from (50 °C to 100 °C) to (240 °C to 260 °C)

NOTE 1 This classification has been defined by the World Health Organization[14].

NOTE 2 Boiling points of some compounds are difficult or impossible to determine because they decompose before they boil at atmospheric pressure. Vapour pressure is another criterion for classification of compound volatility that may be used for classification of organic chemicals[15].

3.3
very volatile organic compound
VVOC
organic compound whose boiling point is in the range from <0 °C to (50 °C to 100 °C)

NOTE 1 This classification has been defined by the World Health Organization[14].

NOTE 2 Boiling points of some compounds are difficult or impossible to determine because they decompose before they boil at atmospheric pressure. Vapour pressure is another criterion for classification of compound volatility that may be used for classification of organic chemicals[15].

3.4
total volatile organic compounds
TVOCs
sum of volatile organic compounds, sampled on Tenax TA®, which elute between and including *n*-hexane and *n*-hexadecane on a non-polar capillary column, detected with a flame ionization detector (TVOC-FID) or mass spectrometric detector (TVOC-MS), and quantified by converting the total area of the chromatogram in that analytical window to a nominal mass using the chromatographic response factor for toluene (toluene equivalents)

NOTE While this part of ISO 16000 specifies the determination of individual VOCs, it is common in practice to generate a single concentration value to characterize the total amount of VOCs present in the air. This value is called the TVOC value (see 11.3 and Clause 13). It should be emphasized that the TVOC value so obtained depends on the sampling and analytical methods used, and therefore should be interpreted taking into account the full description of these methods.

4 Principle

A measured volume of sample air is collected from room air, an emission test chamber (see ISO 16000-9) or an emission test cell (see ISO 16000-10) by drawing through one (or more) sorbent tube containing Tenax TA® sorbent. Volatile organic compounds (VOCs) are retained by the sorbent tube, and the compounds are subsequently analysed in the laboratory. The collected VOCs are desorbed by heat and transferred under inert carrier gas via a cold trap or sorbent trap into a gas chromatograph equipped with a capillary column or columns and a flame ionization detector and/or a mass spectrometric detector.

5 Reagents and materials

5.1 Volatile organic compounds for calibration, of chromatographic quality.

5.2 Dilution solvent, for preparing calibration blend solution for liquid spiking, of chromatographic quality, free from compounds co-eluting with the compound(s) of interest (5.1).

NOTE It is in most cases beneficial to use dilution solvent that is considerably more volatile than the VOCs to be analysed. Methanol most commonly fulfils this criterion. Health and safety data for organic compounds are given, for example, in International Chemical Safety Cards (ICSCs)[24].

5.3 Tenax TA®, particle size 0,18 mm to 0,60 mm (30 mesh to 80 mesh).

Tenax TA® is a porous polymer based on 2,6-diphenyleneoxide. Manufactured Tenax TA® contains quantities of impurities, which shall be removed before using it for VOC sampling. Perform cleaning by thermal conditioning the Tenax TA® under a flow of pure carrier gas. Select cleaning conditions so that no degradation of the polymer occurs, e.g. at a temperature of 300 °C for 10 h using a carrier gas flow rate of 50 ml/min to 100 ml/min for packed sampling tubes. Pack pre-cleaned Tenax TA® into sampling tubes that are tightly sealed and store in a closed, emission-free container. Check the success of the cleaning procedure by performing an analysis of the cleaned sorbent.

NOTE Pre-packed, conditioned (cleaned) and capped sorbent tubes are available commercially.

5.4 Standard atmospheres, of known concentrations of the compound(s) of interest, prepared by a recognized procedure. Methods specified in ISO 6141[1] and the appropriate part of ISO 6145[2] are suitable.

Prepare standard atmospheres equivalent to about 100 µg/m^3. 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.

5.5 Standard sorbent tubes, loaded by spiking from standard atmospheres (5.4), prepared by passing an accurately known volume of the standard 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. For indoor air and test chamber air, load sorbent tubes with e.g. 100 ml, 200 ml, 400 ml, 1 l, 2 l, 4 l or 10 l of the 100 µg/m^3 standard atmosphere selected.

5.6 Calibration blend solutions for liquid spiking.

5.6.1 General. The stability and safe storage times of calibration blend solutions shall be determined. Fresh standard solutions shall be prepared accordingly or if there is evidence of deterioration, e.g. reactions between alcohols and ketones. Appropriate calibration solution concentrations vary depending upon expected target analyte levels in each batch of samples. Examples of solution preparation for a range of applications are given in 5.6.2 to 5.6.6.

5.6.2 Solution containing approximately 10 mg/ml of each liquid component. Introduce 50 ml of dilution solvent into a 100 ml volumetric flask. 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, stopper and shake to mix.

5.6.3 Solution containing approximately 1 000 µg/ml of each liquid component. Introduce 50 ml of dilution solvent into a 100 ml volumetric flask. Add 10 ml of solution 5.6.2. Make up to 100 ml with dilution solvent, stopper and shake to mix.

5.6.4 Solution containing approximately 100 µg/ml of each liquid component. Introduce 50 ml of dilution solvent into a 100 ml volumetric flask. Add 10 ml of solution 5.6.3. Make up to 100 ml with dilution solvent, stopper and shake to mix.

5.6.5 Solution containing approximately 10 µg/ml of each liquid component. Introduce 50 ml of dilution solvent into a 100 ml volumetric flask. Add 10 ml of solution 5.6.4. Make up to 100 ml with dilution solvent, stopper and shake to mix.

5.6.6 Solution containing approximately 1 µg/ml of each liquid component. Introduce 50 ml of dilution solvent into a 100 ml volumetric flask. Add 10 ml of solution 5.6.5. Make up to 100 ml with dilution solvent, stopper and shake to mix.

5.7 Standard sorbent tubes, loaded by spiking, prepared by injecting aliquots of standard solutions on to clean sorbent tubes.

The sampling end of a sorbent tube is fitted to the unheated injection unit of the gas chromatograph (GC) (6.10) through which inert purge gas is passed at 100 ml/min, and a 1 µl to 5 µl aliquot of an appropriate standard solution is injected through the septum. After 5 min, the tube is disconnected and sealed. Prepare fresh standard tubes with each batch of samples.

Introducing liquid standards on to sorbent tubes via a GC injector is considered the optimum approach to liquid standard introduction, as components reach the sorbent bed in the vapour phase. Alternatively, liquid standards may be introduced directly on to the sorbent bed using a syringe (6.3).

Calibration mixtures should be prepared in controlled ambient temperature conditions. Before use, temper the solutions accordingly.

NOTE 1 When preparing standard tubes containing SVOC analytes, efficient transfer is enhanced if the configuration of injector allows the tip of the syringe to make gentle contact with the sorbent retaining mechanism (e.g. gauze or frit) within the tube.

NOTE 2 Standard tubes containing VVOCs are more typically prepared either from standard atmospheres (see 5.4 and 5.5) or from concentrated gas standards sourced commercially. It is appropriate for concentrated gas standards to be introduced to the sampling end of sorbent tubes in a stream of carrier gas via an unheated GC injector.

NOTE 3 If standard tubes are being prepared by introducing aliquots from more than one standard solution or gas, it is appropriate first to introduce the standard containing higher boiling components and to introduce the lightest components last. This minimizes risk of analyte breakthrough during the standard tube loading process.

5.8 Commercial, preloaded standard tubes, certified, are available and can be used for establishing analytical quality control and for routine calibration.

5.9 Inert carrier gas, e.g. He, Ar, N_2. The purity of the carrier gas should permit the detection of an injection of 0,5 ng of toluene.

CAUTION — The quality of the carrier gas is of great importance, as contaminants possibly contained in the gases are enriched in the cold trap together with the substances to be analysed.

6 Apparatus

Ordinary laboratory apparatus and in particular the following.

6.1 Sorbent tubes, of stainless steel or glass, containing at least 200 mg of Tenax TA® sorbent (5.3), with metal screw caps and polytetrafluoroethene (PTFE) ferrules.

Tubes with outside diameter of 6,4 mm (0.25 inch), inside diameter of 5 mm, and of length 89 mm (3.5 inch) fulfil the requirement and are used in many commercial thermal desorbers. Use deactivated glass wool or other suitable mechanism, e.g. stainless steel frit, to retain the sorbent in the tube.

NOTE 1 The unit inch is not allowed in ISO documents; inch equivalents are given for information only.

Pre-cleaned sorbent tubes containing Tenax TA® are available commercially. Alternatively, sorbent tubes can be filled in the laboratory as follows.

Weigh the appropriate amount of adsorbent, using no less than 200 mg of sorbent per tube to maintain the sorption capacity. To pack the tube, insert a plug of deactivated glass wool or a stainless steel gauze into one end of the tube. Transfer the adsorbent into the tube, assisted by suction if desired. Place an additional plug or gauze after the sorbent to retain it in the tube.

NOTE 2 The determination of breakthrough volume is specified in ISO 16017-1:2000, Annex B. Breakthrough volumes are proportional to the dimensions of the sampling tube and quantity of sorbent. As an approximate measure, doubling the bed length while tube diameter is kept constant doubles the safe sampling volume (SSV).

6.2 Sorbent tube unions. For sampling, two sorbent tubes connected in series using metal screw-cap couplings with PTFE ferrules.

6.3 Precision syringes, readable to at least 0,1 µl.

6.4 Sampling pump, fulfilling the requirements of EN 1232[11] or ASTM D3686[10].

6.5 Tubing, of polyethylene (PE) or PTFE, of appropriate diameter, used to ensure a leak-proof fit to both pump and sample tube.

Sampling tubes shall not be used with plastic tubing upstream of the sorbent. Interferences from the tubing can introduce contaminants.

6.6 Flow meter calibrator. Bubble meter or other suitable device for gas flow calibration.

6.7 Gas chromatographic (GC) system, fitted with a flame ionization detector and/or mass spectrometric detector capable of detecting an injection of at least 1 ng of toluene with a signal-to-noise ratio of at least 5 to 1.

6.8 Capillary column. A suitable GC capillary column is selected for separation of analytes in the sample. Bonded 100 % dimethylpolysiloxane columns of 30 m to 60 m, internal diameter 0,25 mm to 0,32 mm and phase thickness 0,25 µm to 0,5 µm are examples of columns proven to be suitable for VOC analysis of indoor air, emission test chamber (in accordance with ISO 16000-9) air, and emission test cell (in accordance with ISO 16000-10) air.

NOTE A dimethylpolysiloxane column, e.g. an HP-1[2)] column, does not separate 3-carene from 2-ethyl-1-hexanol with certain oven programmes, nor does it separate *m*- and *p*-xylenes.

6.9 Thermal desorption apparatus, for the two-stage thermal desorption of the sorbent tubes and transfer of desorbed vapours via an inert gas flow into a GC.

A typical apparatus contains a mechanism for holding the tubes to be desorbed while they are heated and purged simultaneously with inert carrier gas. The desorption temperature and time are adjustable, as is the carrier gas flow rate. The apparatus may also incorporate additional features, such as automatic sample-tube loading, leak testing, and a cold trap or other suitable device to concentrate the desorbed sample. 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 (optional). A conventional gas chromatographic injection unit or equivalent device may be used for preparing calibration standards. This can be used *in situ*, or it can be mounted separately. The injector should be unheated to eliminate risk of heat transfer to the tube and associated risk of analyte breakthrough. The back of the injection unit should be adapted if necessary to fit the sample tube. This can be done conveniently by means of compression coupling with an O-ring seal.

NOTE When preparing standard tubes containing SVOC analytes, efficient transfer is enhanced if the configuration of the injector allows the tip of the syringe to make gentle contact with the sorbent retaining mechanism (e.g. gauze or frit) within the tube.

6.11 Calibration of pump. Calibrate the pump with the sorbent tube assembly in line, using an appropriate external calibrated meter.

2) HP-1 is the trade name of a product manufactured by Agilent, Inc. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named.

7 Conditioning and storage of sorbent tubes

7.1 Conditioning

Prior to each sampling use, condition the pre-cleaned sorbent tubes at 300 °C for 10 min under inert carrier gas at a flow rate of 50 ml/min to 100 ml/min, to remove trace organic volatiles possibly trapped on the tube. Analyse a representative number of conditioned tubes for blank value, using routine analytical parameters, to ensure that the thermal desorption blank is sufficiently small. The sorbent tube blank level is acceptable if artefact peaks are no greater than 10 % of the typical peak areas of the analytes of interest. If the blank is unacceptable, recondition the tubes by repeating the conditioning procedure. If after repeated conditioning the blank is still unacceptable, the tubes shall be refilled (see procedure in 6.1).

7.2 Storage of conditioned sorbent tubes before sampling

Seal conditioned sorbent tubes with metal screw-cap fittings with PTFE ferrules and store in an emission-free container at room temperature. Use conditioned sampling tubes within four weeks. Recondition tubes stored for more than four weeks before sampling.

8 Sampling

8.1 Indoor air sampling

Assemble the sampling line. If more than one tube is used in order to ensure that the breakthrough volume for one tube and the analyte of interest is not exceeded, prepare a tube assembly by joining the tubes in series with a union (6.2). Attach the pump to the sorbent tube or tube assembly with PE or PTFE tubing. Start the pump and note and record the sampling flow rate or register reading, note starting time, temperature and, if necessary for calculation, also atmospheric pressure. An appropriate sampling flow rate is in the range of 50 ml/min to 200 ml/min. At the end of the sampling period, note and record the flow rate or register reading, turn the pump off, and note and record the time, temperature and, if necessary, atmospheric pressure. Disconnect the sampling tube from the sampling line and seal both ends using screw-cap fittings with PTFE ferrules.

If sampling flow rate is determined using an integrated flow-measuring device, e.g. a mass flow meter, connect the sampling tube to the sampling line, start the pump, note and record the time and flow rate or register reading. Note and record temperature and, if necessary, atmospheric pressure. An appropriate sampling flow rate is in the range of 50 ml/min to 200 ml/min. At the end of the sampling period, note and record the flow rate or register reading, turn off the pump, note and register the time the pump was turned off. Disconnect the sampling tube from the sampling line and seal both ends using screw-cap fittings with PTFE ferrules.

Sampling from indoor air shall be performed taking into account the general aspects of sampling strategy as specified in ISO 16000-1.

Sampling flow rates lower than 50 ml/min may be used if the operator finds it necessary, e.g. to enable longer sampling times.

8.2 Test chamber air sampling

Assemble the sampling line. If the sampling flow rate is determined with a calibrator, start the pump, note and record the sampling flow rate. Appropriate sampling flow rate is in the range of 50 ml/min to 200 ml/min. When sampling from an emission chamber, the sampling flow shall not exceed 80 % of the air flow rate of the chamber. Connect the sampling tube to the test chamber outlet or other sampling port of the emission test chamber, note and record the time the tube was connected. Note and record temperature and if necessary atmospheric pressure. At the end of the sampling period, disconnect the sampling tube from the chamber sampling port, note and record the time of disconnection, repeat the sampling flow determination, and turn off the pump. Disconnect the sampling tube from the sampling line and seal both ends using screw cap fittings with PTFE ferrules.

If sampling flow rate is determined by using an integrated flow-measuring device, e.g. a mass flow meter, connect the sampling tube to the sampling line and further to the chamber sampling port, start the pump, note and record the time and flow rate or register reading. Note and record temperature and, if necessary, atmospheric pressure. An appropriate sampling flow rate is in the range of 50 ml/min to 200 ml/min. At the end of the sampling period, note and record the flow rate or register reading, turn off the pump, note and register the time the pump was turned off. Disconnect the sampling tube from the sampling line and seal both ends using screw cap fittings with PTFE ferrules.

8.3 Sampling volumes

SSVs, i.e. amounts of gas that can be sampled without breakthrough of VOCs, are listed in Annex B. In general, the suitable sampling volumes when sampling VOCs from non-industrial indoor air is 1 l to 5 l for sampling tubes with 200 mg of Tenax TA®. In material emission measurements, the material type and age, loading factor and air exchange rate in the chamber determine suitable sampling volumes. The maximum recommended sampling volume, in general, is ≤5 l.

Sampling volume has to be adjusted to the expected concentrations. When sampling unknown concentrations, it is recommended that at least three parallel samples be taken with different sampling volumes. If the analytical result is not dependent on the sampling volume, no breakthrough of the analytes has occurred.

8.4 Storage of loaded samples

Loaded sampling tubes shall be tightly sealed and stored in an emission-free container at ambient room temperature. The effect of storage on loaded VOC from indoor or chamber air is not known, although some data (see Annex C) suggest that they may be stable over several months at room temperature. To avoid possible changes, the samples should be analysed as soon as possible and preferably within four weeks after collection.

8.5 Field blanks

Field blanks shall be Tenax TA® sampling tubes identical to those used for VOC sampling. These tubes are subjected to the same handling procedure in the field as the sample tubes, except for the actual period of sampling. Field blanks shall be marked, stored and analysed in sequence with the actual samples. In a measurement campaign, about 10 % of the samples analysed shall be field blanks. If only a few measurements are performed, at least one field blank shall be prepared and analysed.

9 Analysis

9.1 General

For analysis, VOCs are thermally desorbed from the sampling tubes. Separate the individual VOCs using capillary columns in a gas chromatograph and detect with a flame ionization detector (FID) and mass spectrometric detector (MS) or with MS only. MS can be used for both identification and quantification of compounds, while FID signals alone are used only for compound quantification.

When a flame ionization detector and a mass spectrometric detector are used together for the analysis, the detectors can either be fitted to the same gas chromatograph or to different gas chromatographs. In the latter case, identical sample injection and separation parameters shall be used in both instruments to produce comparable chromatograms.

When the quantification is made using FID, calibration standard mixtures of different concentrations or at least a single level calibrant shall be analysed with each set of samples as a check on system performance.

When using MS for quantification, calibration standard mixtures of at least three, or better, five or seven, different concentrations shall be analysed with each set of samples to update the calibration.

Internal standards, e.g. isotopically labelled compounds, may be used to control the performance of sampling and analysis.

9.2 Thermal desorption

Select desorption time and desorption gas flow rate so that the desorption efficiency for octadecane is better than 95 %. The determination of desorption efficiency is described in ISO 16017-1.

Typical desorption conditions for VOC analysis using a secondary cold trap and sampling tube containing 200 mg to 250 mg Tenax TA® are listed in the following.

Desorption temperature	260 °C to 280 °C

Alternative desorption temperatures may be required if different sorbents are used in the sample tube (e.g. for analysis of VVOCs in accordance with ISO 16017-1 or Annex D, or for quantitative recovery of SVOCs). If a different desorption temperature is used, an explanation shall be included in the test report.

Desorption time	5 min to 15 min
Desorption gas flow rate	30 ml/min to 50 ml/min
Cold-trap high temperature	260 °C to 300 °C
Cold-trap low temperature	−30 °C to +20 °C
Cold-trap sorbent	Tenax TA®
Transfer-line temperature	150 °C to 225 °C
Split ratios	Split ratios between the sample tube and secondary trap and between the secondary trap and analytical column (if applicable) should be selected dependent on expected atmospheric concentration. (See guidance from respective manufacturers of the thermal desorption apparatus.)

NOTE The more volatile VVOCs can break through the cold trap under these conditions and are not quantitatively determined by the analysis (see Annex D for information on how to analyse VVOC and SVOC quantitatively). Alternative sorbents and analytical conditions for accommodating a wider range of compounds are listed in D.6.1.

9.3 Temperature programme

Temperature programming of the analytical column is needed when analysing mixtures of substances showing large differences in boiling points and polarities in order to achieve a good resolution in minimal time.

9.4 Analysis of the samples

Analyse VOC samples preferably within four weeks from sampling. Analyse field blanks and appropriate standards in sequence with the samples. Identify VOCs with MS and quantify them from the FID or MS chromatogram.

10 Identification of single VOCs

For identification of single, non-target VOCs, analyse the samples with MS operating in the scan mode. Identify single VOCs detected in the sample using the mass spectrometer total ion chromatogram and the retention time of the compound. Compare the total ion chromatogram with either the mass spectra of pure compounds or commercially available compilations (libraries) of mass spectra. User-generated libraries may also be used. Correspondence of retention time with a retention time of a compound used for calibration on a single column should not exclusively be regarded as proof of identity.

Identify as many compounds as possible, particularly those representing the 10 highest peaks and those present at concentrations above 2 µg/m^3. A list of VOCs which, according to experience at the time of

publication, are frequently encountered in indoor air and emitted from materials is given in Annex A. A satisfactory level of identification has been achieved if the chromatographic peak areas of identified VOCs when summed correspond to at least two-thirds of the total area of all the peaks in the chromatogram eluting between and including *n*-hexane to *n*-hexadecane.

The selected ion monitoring (SIM) mode of MS operation may also be used. The choice is left to the operator, who shall be aware of the differences between SIM and scan modes.

11 Concentration of analytes in the sampled air

11.1 General

Identified compounds are quantified using their individual response factors when the reference compound is available. In other cases, quantification is reported as a toluene equivalent. Unidentified compounds are quantified using the toluene response factor.

11.2 Volatile organic compounds

Compound-specific response factors and the linearity of FID and MS for compounds of interest are determined by calibrating the analytical system with standard solutions (5.5, 5.6.3, 5.6.4, 5.6.5, 5.6.6 or 5.9). Prepare a calibration curve using at least three different concentrations over the linear range (better using five or seven different concentrations). The lowest concentration used for calibration shall be at or below the lowest sample concentration.

The peak areas of a single VOC chromatogram are proportional to the mass of compound injected. For each compound, the relationship between the mass of analyte injected and the corresponding peak area is determined. The slope of the calibration curve over the linear range is the response factor of the VOC studied:

$$A_{\mathrm{St}} = b_{\mathrm{St}} m_{\mathrm{St}} + c_{\mathrm{St}} \tag{1}$$

where

A_{St} is the analyte peak area, in area units, in the chromatogram of the standard;

b_{St} is the slope of the calibration curve;

m_{St} is the mass, in nanograms, of analyte in the standard;

c_{St} is the ordinate intersect of the calibration curve — if the calibration curve passes through the origin, $c_{\mathrm{St}} = 0$.

The mass of analyte, m_{A}, in nanograms, present in the sample is calculated from the detector peak area using the response factor of the analyte:

$$m_{\mathrm{A}} = \frac{A_{\mathrm{A}}}{b_{\mathrm{St}}} - c_{\mathrm{A}} \tag{2}$$

where

A_{A} is the peak area, in area units, of analyte in the chromatogram of the sample;

b_{St} is the slope of the calibration curve;

c_{A} is the ordinate intersect of the calibration curve — if the calibration curve passes through the origin, $c_{\mathrm{A}} = 0$.

The mass concentration, ρ_A, in micrograms per cubic metre, of VOCs identified in the air sampled is calculated by means of Equation (3):

$$\rho_A = \frac{m_A - m_{A0}}{V} \quad (3)$$

where

m_A is the mass, in nanograms, of analyte present in the sampling tube;

m_{A0} is the mass, in nanograms, of analyte present in the blank tube;

V is the sampling volume, in litres.

If necessary, the concentrations are adjusted to 23 °C and 101,3 kPa:

$$\rho_{A;101,3;296} = \rho_A \frac{101,3}{p} \frac{(t + 273)}{296} \quad (4)$$

where

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

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

Unidentified compounds in the sample are quantified using the calibration response factor for toluene.

11.3 Total volatile organic compounds

The TVOC concentration is determined as follows.

Consider the entire area of the chromatogram between *n*-hexane and *n*-hexadecane. Using the toluene response factor, convert the area into mass units of toluene. Using Equation (3), calculate the TVOC mass concentration in the sampled air. To take account of the background, determine the TVOC value of the blank tube using the same procedure and subtract this from the sample TVOC result to give a corrected TVOC value.

The parameters of a “standard spectra tune”, or equivalent MS parameters, shall be set when using MS for this purpose. Otherwise, the use of an FID is preferred.

NOTE 1 These recommendations are given to improve the comparability of TVOC results.

NOTE 2 TVOC determined in toluene equivalents is semi-quantitative, since individual compounds in the mixture can have response factors varying widely from the toluene response factor.

11.4 VVOC and SVOC compounds observed outside the TVOC range

To obtain information on additional organic compounds present in indoor air or emitted from products into test chamber air, it is appropriate not only to determine VOC but also to have some information on VVOC and SVOC, i.e. organic compounds eluted before *n*-hexane and after *n*-hexadecane. For this, follow guidance in Annex D.

12 Performance characteristics

Before this method is used, its performance characteristics should be determined in accordance with ISO/IEC Guide 98-3[9]. This determination should include, as a minimum, the estimation of uncertainty components from the following sources:

a) sampling:
   1) flow,
   2) time,
   3) temperature,
   4) pressure,
   5) sampling efficiency;

b) sampling integrity:
   1) measure and stability,
   2) blank stability;

c) desorption efficiency;

d) calibration:
   1) standards,
   2) lack-of-fit of calibration function;

e) analysis:
   1) repeatability,
   2) blank level;

f) environmental influences:
   1) temperature at sampling,
   2) humidity at sampling,
   3) interferents;

g) field repeatability;

h) chamber techniques:
   1) air change,
   2) test specimen preparation.

The accuracy and repeatability of the measuring method are important factors, which shall be determined in order to evaluate the results and the suitability of the method for the intended purposes. The accuracy of the VOC measurement method can be determined if atmospheres of known level (micrograms per cubic metre) can be reliably produced. This is relatively difficult and therefore most researchers only determine the repeatability of their measuring method by repeated sampling from a constant atmosphere.

In a study of chlorinated butadienes in indoor air, the uncertainty of the measurement results was assessed based on the principles of ISO/IEC Guide 98-3[9]. The combined relative uncertainty for the measurement of

hexachlorobutadiene at a volume fraction level of $0{,}6 \times 10^{-9}$ was ±12 % and the expanded relative uncertainty (at the 95 % confidence level) was ±23 %[16].

The repeatability of sampling of non-polar hydrocarbons from cylinder atmospheres containing six VOCs has been reported [17]. For 2 l samples, the repeatability for Tenax TA® was less than 10 %, and for 0,5 l samples it was 12 %.

NOTE In material emission testing, interlaboratory comparisons have been organized to assess the agreement between laboratories undertaking tests to characterize the emission of VOCs from indoor materials and products. The results of these intercomparisons have been published[18][19].

13 Test report

The test report shall contain at least the following information:

a) purpose of the measurements;

b) description of the sampling location;

c) time and date of the sampling;

d) sampling conditions (temperature, relative humidity);

e) reference to this part of ISO 16000 (ISO 16000-6:2011);

f) full description of the sampling procedure;

g) full description of the analytical procedure;

h) detection and quantification limits of the analytical method;

i) concentrations of identified compounds, provided with CAS numbers, including calculation and calibration principles used;

j) uncertainty of the reported results.

The results can be complemented by $TVOC_{FID}$ or $TVOC_{MS}$ mass concentration in toluene equivalents.

14 Quality control

An appropriate level of quality control shall be employed, including verification of the following.

a) Field blanks are prepared in accordance with 8.5.

b) The sorbent tube blank level is acceptable if artefact peaks are no greater than 10 % of the typical peak areas of the analytes of interest.

c) Desorption efficiency of VOCs can be determined as described in ISO 16017-1 and should be better than 95 %. Some additional advice on checking desorption efficiency is given in D.5.2.

d) The collection efficiency can be controlled by using back-up tubes or taking samples of different sampling volumes less than the safe sampling volume.

e) Repeatability of the measuring method has been determined, e.g. using collection and analysis of duplicate samples. The duplicate samples should agree within 15 %.

The recovery of hydrocarbons eluting in the *n*-hexane to *n*-hexadecane chromatographic range has been shown to be better than 95 %.

Annex A
(informative)

Examples of compounds detected in indoor air and from building products in test chambers

Table A.1 — Examples of compounds detected in indoor air and emitted from building products in test chambers[20][21]

Chemical compound	CAS No.	Boiling point °C
Aromatic hydrocarbons		
1,2,3-Trimethylbenzene	526-73-8	176
1,2,4,5-Tetramethylbenzene	95-93-2	197
1,2,4-Trimethylbenzene	95-63-6	169
1,3,5-Trimethylbenzene	108-67-8	165
1,3-Diisopropylbenzene	99-62-7	203
1,4-Diisopropylbenzene	100-18-5	203
1-Methyl-2-propylbenzene	1074-17-5	
1-Methyl-3-propylbenzene	1074-43-7	175
1-Propenylbenzene	637-50-3	175
2-Ethyltoluene	611-14-3	165
3-Ethyltoluene/4-ethyltoluene	620-14-4/622-96-8	162
2-Phenyloctane	777-22-0	123
4-Phenylcyclohexene	4994-16-5	251[a]
5-Phenyldecane	4537-11-5	
5-Phenylundecane	4537-15-9	
α-Methylstyrene	98-83-9	165
Benzene	71-43-2	80
Ethylbenzene	100-41-4	136
Ethylylbenzene/Ethynylbenzene	536-74-3	144
Isopropylbenzene	98-82-8	152
m-/*p*-Methylstyrene	100-80-1/622-97-9	168/169
m-/*p*-Xylene	108-38-3/106-42-3	139/138
Naphthalene	91-20-3	218
n-Butylbenzene	104-51-8	183
n-Propylbenzene	103-65-1	159
o-Methylstyrene	611-15-4	171
o-Xylene	95-47-6	144
Styrene	100-42-5	145
Toluene	108-88-3	111

Table A.1 (*continued*)

Chemical compound	CAS No.	Boiling point °C
Aliphatic hydrocarbons *n*-C_6 to *n*-C_{16}		
1-Decene	872-05-9	171
1-Octene	111-66-0	121
2,2,4,6,6-Pentamethylheptane	13475-82-6	178
2,4,6-Trimethyloctane	62016-37-9	
2-Methylhexane	591-76-4	90
2-Methylnonane	871-83-0	167
2-Methyloctane	3221-61-2	143
2-Methylpentane	107-83-5	60[b]
3,5-Dimethyloctane	15869-93-9	159
3-Methylhexane	589-34-4	92
3-Methyloctane	2216-33-3	143
3-Methylpentane	96-14-0	63[b]
4-Methyldecane	2847-72-5	189
Isododecane	31807-55-3	216
n-Decane	124-18-5	174
n-Dodecane	112-40-3	216
n-Heptane	142-82-5	98
n-Hexadecane	544-76-3	287
n-Hexane	110-54-3	69
n-Nonane	111-84-2	151
n-Octane	111-65-9	125
n-Pentadecane	629-62-9	271
n-Tetradecane	629-59-4	254
n-Tridecane	629-50-5	235
n-Undecane	1120-21-4	196
Cycloalkanes		
1,4-Dimethylcyclohexane	589-90-2	124
1-Methyl-4-methylethylcyclohexane (*cis*/*trans*)	6069-98-3/1678-82-6	167
Cyclohexane	110-82-7	81
Methylcyclohexane	108-87-2	101
Methylcyclopentane	96-37-7	72

Table A.1 (*continued*)

Chemical compound	CAS No.	Boiling point °C
Terpenes		
β-Caryophyllene	87-44-5	275
α-Pinene	80-56-8	156
β-Pinene	18172-67-3	164
3-Carene	13466-78-9	167
α-Cedrene	469-61-4	262
Camphene	79-92-5	158
Limonene	138-86-3	176
Longifolene	475-20-7	254
Turpentine	8006-64-2	150 to 180
Alcohols		
1-Butanol	71-36-3	118
1-Hexanol	111-27-3	158
1-Octanol	111-87-5	194
1-Pentanol	71-41-0	137
1-Propanol	71-23-8	97
2-Ethyl-1-hexanol	104-76-7	182
2-Methyl-1-propanol (isobutanol)	78-83-1	108
2-Methyl-2-propanol	75-65-0	82
2-Propanol	67-63-0	82
2,6-Di-*t*-butyl-4-methylphenol (BHT)	128-37-0	265
Cyclohexanol	108-93-0	161
Phenol	108-95-2	182
2,2,4-Trimethyl-1,3-pentanediol isobutyrate	25265-77-4	254
Glycols and glycol ethers		
1-Methoxy-2-propanol	107-98-2	118
2-Butoxyethanol	111-76-2	171
2-Butoxyethoxyethanol	112-34-5	231
2-Ethoxyethanol	110-80-5	136
2-Methoxyethanol	109-86-4	125
2-Phenoxyethanol	122-99-6	245
3-Phenyl-1-propanol	6180-61-6	235
2-(2-Butoxyethoxy)ethanol	112-34-5	230
Dimethoxyethane	110-71-4	85
Dimethoxymethane	109-87-5	42[b]
Propylene glycol	57-55-6	189

Table A.1 (*continued*)

Chemical compound	CAS No.	Boiling point °C
Aldehydes		
2-Butenal	123-73-9	104
2-Decenal	2497-25-8	
2-Ethylhexanal	123-05-7	163
2-Furancarboxaldehyde	98-01-1	162
2-Heptenal (*cis*/*trans*)	57266-86-1/18829-55-5	90 to 91 at 50 mmHg
2-Nonenal	2463-53-8	100 to 102 at 16 mmHg
2-Pentenal	1576-87-0	115 to 125
2-Undecenal	1337-83-3	
Acetaldehyde	75-07-0	21[b]
Benzaldehyde	100-52-7	179
Butanal	123-72-8	76
Decanal	112-31-2	208
Heptanal	111-71-7	153
Hexanal	66-25-1	129
Nonanal	124-19-6	190
Octanal	124-13-0	171
Pentanal	110-62-3	103
Propanal	123-38-6	49[b]
Ketones		
2-Butanone (methyl ethyl ketone)	78-93-3	80
2-Methylcyclohexanone	583-60-8	163
2-Methylcyclopentanone	1120-72-5	139
3-Methyl-2-butanone	563-80-4	95
4-Methyl-2-pentanone (methyl isobutyl ketone)	108-10-1	117
3,5,5-Trimethylcyclohex-2-enone	78-59-1	214
Acetone	67-64-1	56[b]
Acetophenone	98-86-2	202
Cyclohexanone	108-94-1	155
Cyclopentanone	120-92-3	130
Halocarbons		
1,1,1,2-Tetrachloroethane	630-20-6	130
1,1,2,2-Tetrachloroethane	79-34-5	146
1,1,1-Trichloroethane	71-55-6	74
1,1,2-Trichloroethane	79-00-5	114
1,2-Dichloroethane	107-06-2	84
1,4-Dichlorobenzene	106-46-7	173

Table A.1 (*continued*)

Chemical compound	CAS No.	Boiling point °C
Carbon tetrachloride	56-23-5	76
Chlorobenzene	108-90-7	131
Dichloromethane	75-09-2	40[b]
Tetrachloroethene	127-18-4	121
Trichloroethene	79-01-6	87
Acids		
2,2-Dimethylpropanoic acid	75-98-9	164
Acetic acid	64-19-7	118
Butyric acid	107-92-6	163
Heptanoic acid	111-14-8	223
Hexadecanoic acid	57-10-3	350
Hexanoic acid	142-62-1	202
Isobutyric acid	79-31-2	153
Octanoic acid	124-07-2	240
Pentanoic acid	109-52-4	186
Propanoic acid	79-09-4	141
Esters		
2-Ethoxyethyl acetate	111-15-9	156
2-Ethylhexyl acetate	103-09-3	198
2-Methoxyethyl acetate	110-49-6	145
Butoxyethyl acetate	112-07-2	192
Butyl acetate	123-86-4	126
Butyl formate	592-84-7	107
Ethyl acetate	141-78-6	77
Ethyl acrylate	140-88-5	100
Isobutyl acetate	110-19-0	118
Isopropyl acetate	108-21-4	90
Linalool acetate	115-95-7	220
Methyl acrylate	96-33-3	81
Methyl methacrylate	80-62-6	100
Propyl acetate	109-60-4	102
2,2,4-Trimethylpentanediol diisobutyrate	6846-50-0	281
Vinyl acetate	108-05-4	72[b]
Dibutyl phthalate	84-74-2	340
Dimethyl phthalate	131-11-3	284

Table A.1 (*continued*)

Chemical compound	CAS No.	Boiling point °C
Other		
1,4-Dioxane	123-91-1	101
1-Methyl-2-pyrrolidinone	872-50-4	202
2-Pentylfuran	3777-69-3	>120
Aniline	62-53-3	184
Caprolactam	105-60-2	267
Indene	95-13-6	182
Nitrobenzene	98-95-3	211
Pyridine	110-86-1	116
Tetrahydrofuran	109-99-9	67[b]

NOTE 1 Safe sampling volumes for organic vapours are given in Annex B.

NOTE 2 When analysing VOCs eluting before *n*-hexane, the complementary sorbents given in ISO 16017-1 can be used.

[a] Value of 1-phenylcyclohexene.

[b] Compounds with boiling points below that of hexane are not retained quantitatively by Tenax TA® when using the sampling tube size and sampling volumes recommended in this part of ISO 16000.

Annex B
(informative)

Safe sampling volumes for selected organic vapours sampled on Tenax TA®

Table B.1 provides data on extrapolated retention volumes and SSVs for organic vapours sampled on a 200 mg Tenax TA® sorbent tube at 20 °C [12][15][22][23]. CAS numbers of the compounds are listed in Table A.1.

Table B.1 — Safe sampling volumes for organic vapours sampled on Tenax TA®

Organic compound	Boiling point °C	Vapour pressure kPa (25 °C)	Retention volume l	SSV 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	0,5	1 400	700	3 500	150
Decane	174	0,13	4 200	2 100	$1,0 \times 10^4$	160
Undecane	196	0,14	$2,5 \times 10^4$	$1,2 \times 10^4$	$6,0 \times 10^4$	170
Dodecane	216	0,04	$1,26 \times 10^5$	$6,3 \times 10^4$	$3,0 \times 10^5$	180
Benzene	80	10,1	13	6,2	31	120
Toluene	111	2,9	76	38	190	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	0,3	1 700	850	4 000	160
Isopropylbenzene	152	0,4	960	480	2 400	160
Ethyltoluene	162	—	2 000	1 000	5 000	160
Trimethylbenzene	165 to 176	0,15 to 0,2	3 600	1 800	8 900	170
Styrene	145	0,88	600	300	1 500	160
Methylstyrene	167	0,3	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 TA®			
1,1,2-Trichloroethane	114	2,5	68	34	170	120
1,1,1,2-Tetrachloroethane	130	0,6 to 0,7	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

Table B.1 (*continued*)

Organic compound	Boiling point °C	Vapour pressure kPa (25 °C)	Retention volume l	SSV 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	1,9	170	85	420	150
Isobutyl acetate	115	2,7	265	130	650	130
t-Butyl acetate	98	—	Not recommended on Tenax TA®			
Methyl acrylate	81	9 to 11	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	1,2 (20 °C)	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						
2-Butanone (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 TA®			
Octanol	180	<0,1	2 800	1 400	7 000	160
Phenol	182	0,03	480	240	1 200	190
Others						
Pyridine	116	16	8	40	150	—
Aniline	184	0,09	440	220	1100	190
Nitrobenzene	211	0,02	28 000	14 000	70 000	200

Annex C
(informative)

Storage recovery of solvents on Tenax TA® sorbent tubes

Table C.1 provides data on storage recovery of solvents on Tenax TA® sorbent tubes [ISO 16017-1]. The CAS numbers of the compounds are listed in Table A.1.

Table C.1 — Solvent recovery after storage on Tenax TA® sorbent tubes

Organic compound	Loading	Storage time 5 months		Storage time 11 months	
		Mean recovery[a]	Precision (coefficient of variation)	Mean recovery	Precision (coefficient of variation)
	µg	%	%	%	%
Hydrocarbons					
Hexane	7,8	93,6	17,9	100,8	26,1
Heptane	8,4	99,5	2,1	100,0	1,3
Octane	8,6	100,1	1,8	100,0	0,5
Nonane	12,0	Nd	Nd	101,0	0,4
Decane	9,2	100,4	1,5	100,2	0,5
Undecane	9,1	100,7	1,5	100,2	0,2
Dodecane	9,9	101,8	1,5	101,5	0,4
Benzene	11,0	98,7	2,0	98,6	0,8
Toluene	10,9	(100,0)	1,8	(100,0)	0,6
p-Xylene	5,3	99,9	1,7	99,8	0,7
o-Xylene	11,0	100,0	1,7	98,8	0,7
Ethylbenzene	10,0	99,6	0,4	97,9	1,3
Propylbenzene	10,5	99,7	1,5	98,5	0,7
Isopropylbenzene	10,9	98,9	1,8	97,2	1,3
m+*p*-Ethyltoluene	10,5	98,8	1,7	96,9	1,2
o-Ethyltoluene	5,4	100,1	1,6	98,9	0,7
1,2,4-Trimethylbenzene	10,8	100,1	1,3	99,1	0,5
1,3,5-Trimethylbenzene	10,7	100,0	1,5	99,1	0,5
Trimethylbenzene	10,2	101,6	0,5	101,3	0,8

Table C.1 (*continued*)

Organic compound	Loading	Storage time 5 months		Storage time 11 months	
		Mean recovery[a]	Precision (coefficient of variation)	Mean recovery	Precision (coefficient of variation)
	µg	%	%	%	%
Esters and glycol ethers					
Ethyl acetate	10,3	97,6	1,0	100,0	2,5
Propyl acetate	10,9	100,5	1,7	99,1	0,8
Isopropyl acetate	9,4	97,0	0,4	100,0	1,4
Butyl acetate	10,8	100,3	1,6	99,9	0,6
Isobutyl acetate	10,7	100,2	1,4	99,8	0,7
Methoxyethanol	8,9	87,3	5,7	93,1	1,6
Ethoxyethanol	10,4	97,6	2,5	97,2	3,3
Butoxyethanol	10,0	100,6	4,1	100,1	3,0
Methoxypropanol	10,4	95,3	3,6	99,0	1,2
Methoxyethyl acetate	12,5	100,6	1,4	98,9	1,4
Ethoxyethyl acetate	11,4	99,8	2,2	98,7	2,6
Butoxyethyl acetate	11,5	101,3	1,3	99,9	1,1
Aldehydes and ketones					
2-Butanone (methyl ethyl ketone)	9,2	97,4	0,8	99,1	0,6
Methyl isobutyl ketone	9,3	100,7	0,6	100,7	0,5
Cyclohexanone	10,9	102,4	1,2	100,7	0,6
2-Methylcyclohexanone	10,7	101,1	0,5	101,1	1,3
3-Methylcyclohexanone	10,5	103,6	1,0	103,0	0,7
4-Methylcyclohexanone	10,6	103,6	1,4	102,7	0,6
3,5,5-Trimethylcyclohex-2-enone	10,6	101,4	0,9	97,7	1,2
Alcohols					
Butanol	9,0	94,8	3,0	96,9	1,2
Isobutanol	8,9	93,6	3,5	96,4	1,0

[a] Normalized to toluene = 100.

Annex D
(informative)

Determination of very volatile and semi-volatile organic compounds in conjunction with volatile organic compounds

D.1 Introduction

This annex describes procedures for sampling and measurement of VVOC and SVOC emissions in conjunction with VOC emissions from building materials in test chambers and cells. VVOC and SVOC compounds are conventionally regarded as those eluting before *n*-hexane and after *n*-hexadecane respectively on a non-polar (polydimethylsiloxane) column.

This annex makes use of guidance provided in ISO 16017-1 on the selection and use of appropriate sorbents and analytical conditions for a wide range of vapour-phase organic compounds.

D.2 Principle

A measured volume of air from the emission test chamber or emission test cell is pumped at a controlled flow rate through a tube containing a combination of sorbents arranged in order of increasing sorbent strength. Vapour-phase organic chemicals are selectively trapped on the sorbents as the air passes through. During subsequent analysis, retained compounds are desorbed from the tube(s) using heat and a reverse flow of carrier gas. These desorbed analytes are swept via a focusing trap into a GC equipped with a capillary column (or columns) and MS detection, with optional additional FID, where they are identified and measured.

Procedural details for sampling and analysing VVOC and SVOC in conjunction with VOC are as specified in the main body of this part of ISO 16000 except as described in the following.

D.3 Reagents and materials

D.3.1 Examples of sorbents

D.3.1.1 Quartz wool or glass/quartz beads, clean (i.e. the beads do not produce analytically significant artefacts) and not prone to particle formation.

D.3.1.2 Tenax TA®[1)] particle size ~0,2 mm to ~0,5 mm (35 mesh to 80 mesh). Tenax TA® is a porous polymer based on 2,6-diphenyleneoxide.

D.3.1.3 "Carbon black" sorbents, such as Carbopack X®[3)] or Carbograph 5 TD®[4)], particle size 0,25 mm to 0,5 mm (40 mesh to 60 mesh). Hydrophobic carbon sorbents suitable for VVOCs with vapour pressures below those typical for C_4 hydrocarbons.

3) Carbopack X is a trade name of Supelco. This information is given for the convenience of users of this document 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.

4) Carbograph 5 TD is a trade name of Lara. This information is given for the convenience of users of this document 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.

D.3.1.4 Carbon molecular sieve (very strong) sorbents can also be used at the non-sampling end of the tube for trapping VVOCs with vapour pressures above those typical for C_4 hydrocarbons. However, note that these sorbents are not completely hydrophobic. Therefore, if such sorbents are included, the tube needs to be dry purged in the sampling direction before analysis.

D.3.2 Preparation of standard tubes

Standard tubes are prepared by introducing liquid or gas-phase standards to the sampling end of conditioned sorbent tubes in a stream of 50 ml/min to 100 ml/min carrier gas as specified in 5.4.

Liquid standards should be prepared in a solvent that is either unretained by the strongest sorbent present in the tube (methanol is a common example) or in a solvent that is readily resolved (chromatographically) from key compounds of interest. If a large proportion of solvent is retained by the sorbent tube during liquid standard addition, minimize the injection volume, e.g. to 1 µl or less.

If the range of compounds of interest requires both gas phase and liquid phase standards, the liquid standard should be introduced first and the solvent purged as required. The gas-phase standard should then be introduced. Ensure that breakthrough volumes are not exceeded during standard addition.

D.4 Apparatus

D.4.1 Stainless steel, inert-coated steel or glass tubes, packed with one or more sorbents. Tubes of the dimensions specified in 6.1 may be packed with up to three sorbents to extend the target analyte volatility range. Multiple sorbents have to be arranged in discreet beds (bands) in order of increasing sorbent strength from the sampling end of the tube (see Figure D.1).

A mass of 200 mg Tenax TA® is used for VOC sampling and analysis and is also compatible with quantitative measurement of the vapour-phase fraction of some higher boiling compounds, e.g. those boiling up to *n*-C_{22}.

NOTE 1 The density of Tenax TA® is variable. However, 200 mg of Tenax TA® normally occupies ~40 mm depth in a 5 mm bore metal tube and ~60 mm depth in a 4 mm bore glass tube.

The recovery of semi-volatiles (particularly those boiling above *n*-C_{22}) is facilitated by inserting a short (5 mm to 10 mm) bed of loosely packed quartz wool in front of the 200 mg of Tenax TA®.

Quantitative sampling and analysis of VVOC can be achieved by adding a 20 mm bed of a suitable stronger sorbent after the Tenax TA®.

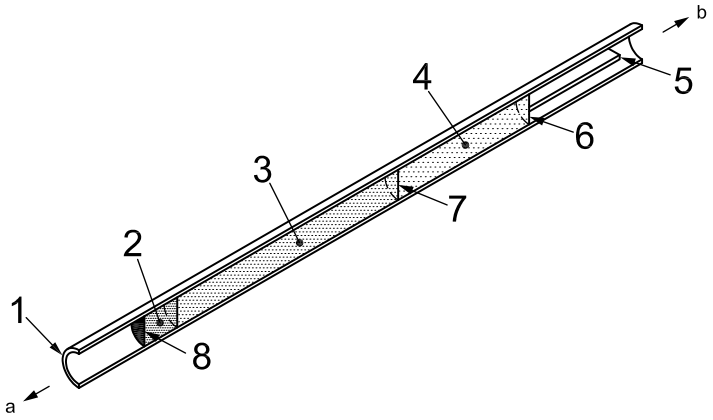
NOTE 2 Selection of Carbopack X® or Carbograph 5 TD® as the stronger sorbent facilitates quantitative retention and analysis of compounds as volatile as 1,3-butadiene, but without significant retention of water from the chamber air or cell air.

NOTE 3 Alternative, even stronger sorbents are available (e.g. carbon molecular sieves) which allow ultra-volatile compounds such as C_3 hydrocarbons and vinyl chloride to be trapped. However, tubes packed with such very strong sorbents are prone to some water retention (see ISO 16017-1) and normally require an additional dry purge step prior to thermo(TD)-GC/MS(FID) analysis.

NOTE 4 Stainless steel or coated stainless steel (metal) tubes of bore 5 mm have capacity for both 200 mg of Tenax TA® and 20 mm of a stronger sorbent.

NOTE 5 It is possible to pack one metal tube with all three sorbents without significantly affecting the mass of Tenax TA®. An example combination is: quartz wool (5 mm); Tenax TA® (175 mg, ~35 mm); and 20 mm of Carbograph 5 TD® or Carbopack X®. All sorbents have to be held within the central (typically 60 mm) portion of the tube, i.e. the portion that is in direct contact with the tube desorption oven of the apparatus (see Figure D.1).

NOTE 6 All sorbent tubes should be desorbed with the flow of carrier gas in the reverse direction to the flow of air during sampling (see Figure D.1).



Key

1 stainless steel or coated steel tube
2 5 mm quartz wool
3 ~35 mm, 175 mg Tenax TA®
4 20 mm stronger sorbent, e.g. Carbograph 5TD or Carbopack X
5 gauze retaining spring
6 sorbent retaining gauze
7 sorbent retaining gauze or 0,5 mm quartz wool
8 sorbent retaining gauze

[a] Desorption gas flow.

[b] Sampling air flow.

Figure D.1 — Example of a metal tube packed with multiple sorbents for extending the target volatility range

NOTE 7 Determination of the breakthrough volume is specified in ISO 16017-1:2000, Annex B. Breakthrough volumes or retention volumes are used as a measure of sorbent strength (affinity) for organic vapours. They are dependent on temperature and are proportional to the dimensions of the sampling tube and quantity of sorbent. Typically, the SSV is set at 2/3 of the breakthrough volume. As an approximate measure, doubling the bed length while tube diameter is kept constant doubles the breakthrough volume. Similarly, as an approximate measure, a rise of 10 °C in the temperature of the tube during sampling, halves the breakthrough volume. Note that most breakthrough volume and safe sampling volume data (e.g. in Annex B and in ISO 16017-1:2000) are reported at 20 °C.

NOTE 8 Optimum pump flow rates for multi-sorbent tubes of the dimensions described are in the range 20 ml/min to 100 ml/min.

NOTE 9 Inert-coated stainless steel or glass tubes are preferred for monitoring reactive, odorous compounds.

An alternative approach is to use tubes containing single sorbents of increasing strength connected together in series with the tube containing the weakest sorbent first in line. However, this is an inefficient approach with regard to the resources required for sampling and analysis.

Pre-packed as well as pre-packed and preconditioned sorbent tubes are available commercially. Alternatively, sorbent tubes can be filled in the laboratory as specified in 6.1.

D.4.2 Capillary GC column. Follow the specifications given in 6.8. Thicker film and/or longer capillary columns may be required if VVOCs are of interest.

D.4.3 Thermal desorption apparatus. Simultaneous analysis of compounds covering a wide volatility range, VVOCs, VOCs, and SVOCs, is facilitated by using more than one sorbent. These are used in series in order of increasing strength, both in the sample tube and in the focusing trap, and by using backflush desorption. Backflush means that the flow of gas used to desorb the sample from the sorbent tube or focusing trap have to be in the reverse direction to that used during sampling or trapping. In this way, higher boiling

compounds are trapped on and released (desorbed) from the front (weaker) sorbents and never come into contact with the rear (stronger) sorbents.

D.5 Sampling test chamber or test cell air

D.5.1 General

Ensure that the sample tube is at approximately the same temperature as the chamber air to prevent risk of water condensation inside the sample tube when sampling emissions from humid samples.

D.5.2 Storage of sampled tubes

Tubes have to be capped immediately after sampling, placed in an airtight emission-free container and stored in a clean area. Tubes packed with a single sorbent can be stored at room temperature. Sampled multi-sorbent tubes require storage under refrigerated conditions to minimize risk of analyte migration within the tube. Analyse tubes as soon as possible and within four weeks.

Long-term storage caps on refrigerated sample tubes should be retightened once the sample has reached its minimum storage temperature.

Refrigerated sample tubes should be allowed to equilibrate with room temperature before they are opened for analysis.

NOTE Information on recovery of VOCs from sorbent tubes after storage is given in this part of ISO 16000 and in ISO 16017-1.

D.6 Analysis

D.6.1 Analytical conditions

When analysing compounds encompassing a wide range of volatility, it is particularly important to ensure that desorption efficiency exceeds the minimum requirement (i.e. >95 %) for each compound. Example test conditions are:

Desorption temperature	200 °C to 320 °C
Desorption time	5 min to 15 min
Desorption gas flow rate	20 ml/min to 50 ml/min
Cold-trap high temperature	250 °C to 330 °C
Cold-trap low temperature	−150 °C (cryofocusing TD systems) −30 °C to +30 °C (sorbent in trap)
Cold-trap sorbent	quartz/Tenax TA®/carbon black (or carbon molecular sieve)
Transfer-line temperature	150 °C to 220 °C
GC oven programme	35 °C to 40 °C for 5 min, 5 °C/min to 10 °C/min to 300 °C, 300 °C for 5 min

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 vapour concentration. (See information from the manufacturer of the thermal desorption apparatus.)

NOTE It may be necessary to set lower desorption temperatures and lower flow path temperatures (e.g. 80 °C to 120 °C) in order to ensure quantitative recovery and analysis of reactive, odorous species such as mercaptans and amines.

As in the case of the sample tube, use of a series of sorbents of increasing strength in the focusing trap extends the volatility range of analytes that can be measured in one run. Backflush trap desorption is required.

To minimize artefacts, tube conditioning and cleaning temperatures should normally be set 10 ºC to 20 ºC above the analytical desorption temperature, but without exceeding the maximum temperature of the least thermally stable sorbent in the tube.

D.6.2 Checking desorption efficiency

Desorption efficiency can be determined either using the procedure specified in ISO 16017-1 or by carrying out a sequence of repeat TD-GC/MS/FID analyses of a single standard. For the latter approach, the split effluent from the desorber [i.e. split effluent during primary (tube) desorption and/or secondary (trap) desorption] is quantitatively re-collected on to a conditioned sorbent tube that is identical to that used for vapour collection. When the re-collected sample is analysed, any split effluent is again re-collected. This allows a sequence of repeated analyses to be carried out on a single standard. If any compound exhibits lower than expected recovery (relative to the split ratio and/or to the recovery of other compounds in the standard) as the sequence proceeds, this indicates poor desorption efficiency for those compounds.

D.7 Determining the concentration of emitted vapours in chamber air or cell air

VVOCs and SVOCs may be quantified in the same analysis as VOCs, provided appropriate steps are taken during sampling and analysis as described in this annex. Key points include:

a) use of an appropriate sorbent or series of sorbents in the sampling tube (see D.4.1);

b) use of an appropriate sorbent or series of sorbents in the focusing trap (see D.6.1);

c) selection of a GC column and GC analytical conditions compatible with the extended analyte volatility range (see D.4.2 and D.6.1).

Sampling and analytical performance for compounds outside the TVOC range can be verified using the checks described for VOCs, see Clause 14.

NOTE 1 Use of three sorbents, quartz wool, Tenax TA® and a strong carbon black (as described in D.4.1 and Figure D.1), in both the sample tube and focusing trap, together with backflush desorption, allows simultaneous quantitative analysis of compounds ranging in volatility from *n*-C_4 to *n*-C_{26} and above. These sorbents are hydrophobic so do not increase risk of water interference when testing emissions from humid products or materials, provided the normal precautions against condensation, described in D.4, are taken.

NOTE 2 More guidance on sorbent selection for sampling over a wide volatility range is given in ISO 16017-1.

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