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Indoor air —

Part 6: Determination of organic compounds (VVOC, VOC, SVOC) in indoor and test chamber air by active sampling on sorbent tubes, thermal desorption and gas chromatography using MS or MS FID

Air intérieur —

Partie 6: Dosage des composés organiques (COTV, COV, COSV) dans l'air intérieur et l'air de chambre d'essai par prélèvement actif sur tubes à sorbant, désorption thermique et chromatographie en phase gazeuse avec détection 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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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

This third edition cancels and replaces the second edition (ISO 16000-6:2011), which has been technically revised. The main changes compared to the previous edition are as follows:

- other sorbents than Tenax TA® are allowed to be used;
- descriptions of VVOC and SVOC measurements are included in the mandatory part of the document.

A list of all parts in the ISO 16000 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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 measuring vapour-phase organic chemicals in air.

This document can be applied to measure vapour phase organic compounds in indoor environments that include buildings with varying designs and purposes and cabins for different modes of transport, as well as measurement in product emission test chambers. These measurements can be for a range of purposes as described in ISO 16000-1 and ISO 16000-5, therefore the requirement for the measurement may be well defined by the task descriptor or may be quite open. For example, the task may be to determine a specific list of target chemicals with a defined sampling time and sensitivity of measurement or it may be to investigate the cause of a reported and poorly understood indoor air quality problem. Depending upon the task of measurement the user of this document should select the most appropriate sampling and analytical instrumentation and conditions. This document provides that information in the normative part combined with informative guidance. Figure 1 refers to the most critical parts of the standard with regard to selection of the most appropriate methodology for the task to be undertaken. Tenax TA®1) only or multisorbents can be used to capture ranges of vapour phase organic compounds. Multisorbents are used for wider ranges and may improve recovery of compounds.

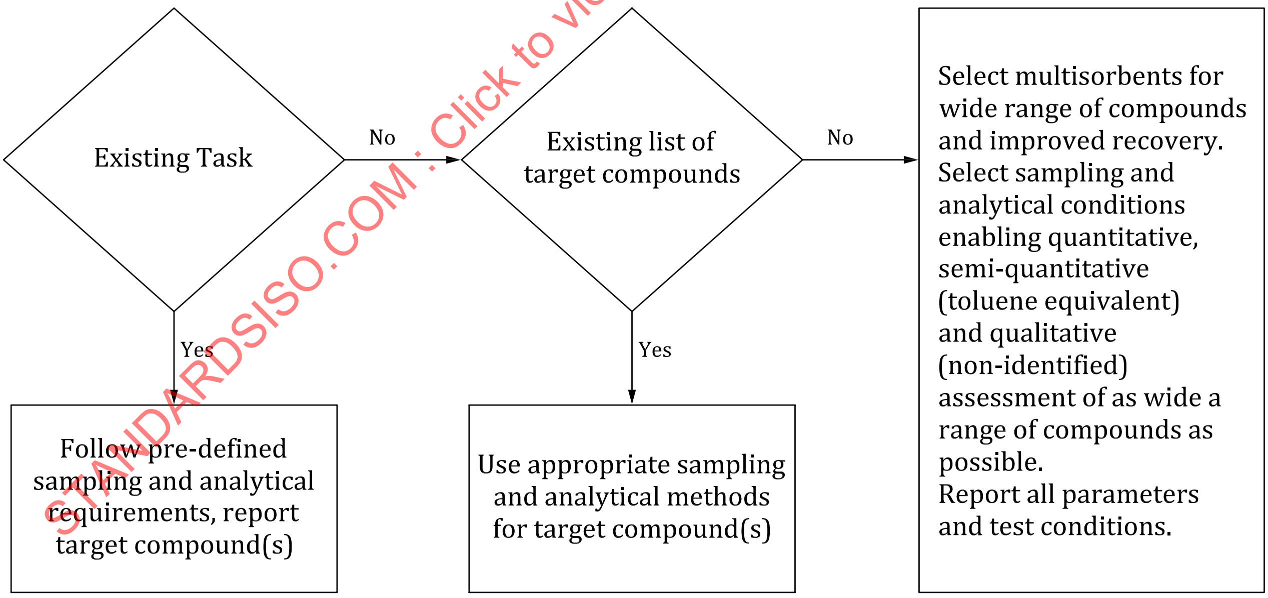

Figure 1 — Measurement scheme showing different ways of analysing air samples depending on the respective task including target compounds

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1) Tenax TA® is a 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.

Indoor air —

Part 6:
Determination of organic compounds (VVOC, VOC, SVOC) in indoor and test chamber air by active sampling on sorbent tubes, thermal desorption and gas chromatography using MS or MS FID

1 Scope

This document specifies a method for determination of volatile organic compounds (VOC) in indoor air and in air sampled for the determination of the emission from products or materials used in indoor environments (according to ISO 16000-1) using test chambers and test cells. The method uses sorbent sampling tubes with subsequent thermal desorption (TD) and gas chromatographic (GC) analysis employing a capillary column and a mass spectrometric (MS) detector with or without an additional flame ionisation detector (FID)[13].

The method is applicable to the measurement of most GC-compatible vapour-phase organic compounds at concentrations ranging from micrograms per cubic metre to several milligrams per cubic metre. Many very volatile organic compounds (VVOC) and semi-volatile organic compounds (SVOC) can be analysed depending on the sorbents used.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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*

EN 13137, *Workplace atmospheres – Pumps for personal sampling of chemical and biological agents – Requirements and test methods*

3 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
semi-volatile organic compound
SVOC
organic compound eluting after n-hexadecane on a gas chromatographic column specified as a 5 % phenyl 95 % methyl polysiloxane phase capillary gas chromatographic column

Note 1 to entry: The vapour-fraction of SVOC ranging in volatility to n-C_{44} can also be analysed by thermal desorption GC-MS but requires specific sampling and analytical conditions for optimum performance [22,25].

3.2
volatile organic compound
VOC
organic compound eluting between and including n-hexane and n-hexadecane on a gas chromatographic column specified as a 5 % phenyl 95 % methyl polysiloxane phase capillary gas chromatographic column

3.3
very volatile organic compound
VVOC
organic compound eluting before n-hexane on a gas chromatographic column specified as 5 % phenyl 95 % methyl polysiloxane phase capillary gas chromatographic column

3.4
total volatile organic compounds
TVOC
sum of the concentration of the identified and unidentified *volatile organic compounds* (3.2) calculated as detailed in Annex A

3.5
total semi-volatile organic compounds
TSVOC
sum of the concentrations of identified and unidentified *semi-volatile organic compounds* (3.1) and calculated as detailed in Annex A

Note 1 to entry: The limit of volatility of SVOCs included in the TSVOC sum may be defined by the specific task list.

3.6
target compound
individual vapour phase compound in indoor air with a concentration determined quantitatively and reported as a result of this method

3.7
task list
specific list of requirements for sampling and analysis defined prior to testing and reflected in the reporting of the results

Note 1 to entry: The requirements may include a specific target list with or without associated limit criteria, and/or require investigations of unknowns. They may also include particular control of aspects such as the location, duration and frequency of sampling.

3.8
laboratory blank
conditioned sorbent tube from the batch selected for each sampling exercise, retained in the laboratory, sealed with long term storage caps throughout the sampling exercise to be used as a blank tube

Note 1 to entry: These tubes are analysed with the sampled tubes.

3.9
field blank
conditioned sorbent tube from the batch used for the sampling exercise, subjected to the same handling procedure in the field as the sample tubes, including removal and replacement of storage caps, but not used for sample collection

3.10
internal standard
compound of known concentration added to a sample to facilitate the qualitative identification and/or quantitative determination of the sample components

4 Abbreviated terms

For the purpose of this document, the following abbreviated terms apply:

FID	flame ionisation detector
GC	gas chromatograph
MS	mass spectrometer
SVOC	semi-volatile organic compounds
TD	thermal desorption
TIC	total ion chromatogram
TSVOC	total semi-volatile organic compounds
TVOC	total volatile organic compounds
VOC	volatile organic compounds
VVOC	very volatile organic compounds

5 Principle

A measured volume of sample air is actively collected from indoor air, vehicle interior air, an emission test chamber (see ISO 16000-9, ISO 12219-4, ISO 12219-6) or an emission test cell (see ISO 16000-10) by drawing through one (or more) sorbent tubes. VOC, VVOC and SVOC are retained by the sorbent tube, and the compounds are subsequently analysed in the laboratory to determine the identity, retained mass and associated air concentration of as many individual compounds as required by the specific test. Depending upon the range of target compounds the most appropriate sorbent tube(s), sampling and analytical conditions are applied. The collected compounds are desorbed by heat and transferred under inert carrier gas via a focussing trap into a gas chromatograph equipped with a capillary column and a mass spectrometer, with or without an additional flame ionisation detector (FID).

6 Reagents and materials

6.1 Organic compounds for calibration of chromatographic quality

6.2 Dilution solvent for preparing calibration blend solution for liquid spiking. Shall be of chromatographic quality, free from compounds co-eluting with the compound(s) of interest (6.1)

6.3 Sorbents

6.3.1 General

Multiple sorbents, suitable for thermal desorption, are commercially available. They range in strength from very retentive sorbents required to retain and release VVOC to very weak sorbents suitable for quantitative sampling and release of SVOC. For particulate sorbents, the relevant particle size is 0,18 mm to 0,60 mm (80 mesh – 30 mesh). For a detailed list of sorbents see Annex D.

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

6.3.3 Porous Polymers, i.e. Tenax TA® particle size approx. 0,25 mm to approx.0,6 mm (60 mesh to 30 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 air sampling.

6.3.4 "Carbon black" sorbents, such as Carbopack X®[2] or Carbograph 5 TD®[3], particle size 0,25 mm to 0,5 mm (60 mesh to 40 mesh). Hydrophobic carbon sorbents suitable for VOC and VVOC with vapour pressures below those typical for C_4 hydrocarbons.

6.3.5 Carbon molecular sieve (very strong) sorbents can also be used at the non-sampling end of the tube for trapping VVOC 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.

6.4 Preparing calibration standards on sorbent tubes

As many identified substances as possible, or as required, should be calibrated using original reference compounds. Standards should be introduced to the sampling end of conditioned sorbent tubes using either liquid or gas phase standards.

6.4.1 Gas-phase standards

Standard atmospheres of known concentrations of the compound(s) of interest, shall be prepared by a recognized procedure such as ISO 6141[1] or ISO 6145[2]. Typical concentrations are around 100 µg/m³ but levels will vary depending on test requirements. Alternatively, gas standards of appropriate quality and concentration shall be sourced commercially.

If the concentrations in any prepared standard atmosphere are not traceable to primary standards and/or if the inertness and stability of the atmospheres generated cannot be guaranteed, the concentration shall be confirmed using an independent procedure.

NOTE Producing gas phase standards of reactive and/or high boiling compounds can be particularly difficult. Frequent monitoring of the standard is needed.

6.4.2 Loading sorbent tubes with gas-phase standards

Pass a known volume of standard atmosphere or gas standard through a conditioned sorbent tube from the sampling end, e.g. by means of a pump operating at 50 ml/min.

The volume of gas-phase standard sampled shall not exceed the breakthrough volume of sorbent tube for any of the compounds of interest.

After loading disconnect and seal the tube. Prepare fresh standards with each batch of samples. For indoor air and emission test chamber studies, 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/m³ standard atmosphere selected.

6.4.3 Calibration blend solution for liquid spiking

Standard solution concentrations will vary depending on test requirements. The selected compound(s) shall be prepared or obtained as a liquid standard in chromatographic-grade solvent (e.g. in methanol) at an appropriate level – typically between 10 ng/µl and 1000 ng/µl – depending on system sensitivity and the analytical conditions selected, for example split ratios. A suitably precise micro-syringe shall

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[2] 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.

[3] 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 the the same results.

be used to introduce 1 µl aliquots of the standard solution onto the sampling end of sorbent tubes in a stream of inert gas as described in 6.4.4. 1 µl is the suggested volume unless solvent can be selectively and efficiently purged without jeopardising breakthrough of the most volatile compound(s) of interest.

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.

6.4.4 Loading sorbent tubes with liquid standards

The sampling end of a sorbent tube is fitted to the unheated injection unit of the gas chromatograph (GC) (see 7.6) through which inert purge gas is passed at 100 ± 10 ml/min, and a maximum 1 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.

NOTE 1 It is more difficult to selectively purge solvent from multi-sorbent tubes, particularly those containing strong sorbents. Smaller injection volumes are recommended for stronger sorbents and multi-sorbent tubes.

Introducing liquid standards onto 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.

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

NOTE 2 When preparing standard tubes from liquid standards 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) at the sampling end of the tube.

NOTE 3 It is important to keep liquid standard injection volumes to 1 µl or less unless the solvent can be selectively purged from the tube prior to analysis. Using small injection volumes minimises the difference between standards and samples during analysis thus minimising uncertainty.

NOTE 4 Standard tubes containing VVOC are more typically prepared either from standard atmospheres (see 6.4.1 and 6.4.5) 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 or similar device.

An internal standard can be added by mixing with the calibration solution or by spiking separately.

NOTE 5 If standard tubes are being prepared by introducing aliquots from more than one standard solution or gas, it is appropriate to first introduce the standard containing higher boiling components and to introduce the most volatile organic compounds last. This minimizes risk of analyte breakthrough during the standard tube loading process.

The purity of the inert carrier gas used to purge sorbent tubes during standard introduction (e.g. He, Ar, N2) should permit the detection of an injection of 0,5 ng toluene. The quality of the carrier gas is of great importance, as any contaminants contained in the gas are enriched on the sorbent together with the substances to be analysed.

Other techniques such as direct liquid spiking onto the sorbent bed without gas stream applied are also possible. In this case it is important to use tubes where the syringe needle can directly reach the sorbent bed.

6.4.5 Commercial, pre-loaded standard tubes

Certified pre-loaded standard tubes are available and can be used for establishing analytical quality control and for routine calibration.

7 Apparatus

Ordinary laboratory apparatus and in particular the following:

7.1 Sorbent tubes of stainless steel or glass,

7.1.1 General

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. Conditioned and sampled sorbent tubes shall be effectively sealed, e.g. with metal screw caps and combined polytetrafluoroethene (PTFE) ferrules. Alternative tube dimensions may be applied if appropriate performance data concerning trapping and recovery of target compounds is available as well as information on safe sampling volumes (SSV).

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

Pre-packed sorbent tubes are available commercially. Alternatively, sorbent tubes can be filled in the laboratory as follows.

Weigh the appropriate amount of each adsorbent in turn into the tube and tap it down gently to settle, assisted by suction if desired. Place an additional plug or gauze after each sorbent to prevent sorbent mixing and retain the sorbents in the tube.

NOTE 2 The determination of breakthrough volume is specified in ISO 16017-1:2000 Annex B. Breakthrough 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 volume data (e.g. in Annex E and in ISO 16017-1:2000) are reported at 20 °C. Note also that the breakthrough volume of some sorbents is adversily affected by high humidity (see ISO 16017-1).

When filling sorbent(s) into tubes, care shall be taken to ensure that the position of the sorbent(s) within the tube corresponds to the position of the tube heater of the instrument used. This ensures direct heating of the sorbent(s), minimising carryover. Contact the instrument manufacturer for details.

7.1.2 Sorbent tubes — Combinations and options

See Annexes C and D for more information.

Tubes of the dimensions described in 7.1.1 may contain up to 3 sorbents as well as quartz (or glass wool), arranged in order, from least retentive to most retentive, from the sampling end. This maximises the target analyte volatility range.

A mass of about 200 mg Tenax TA® is suitable for sampling VOC and 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 less volatile than 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 ng 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 stronger sorbent facilitates quantitative retention and analysis of compounds as volatile as 1,3-butadiene, but without significant retention of water.

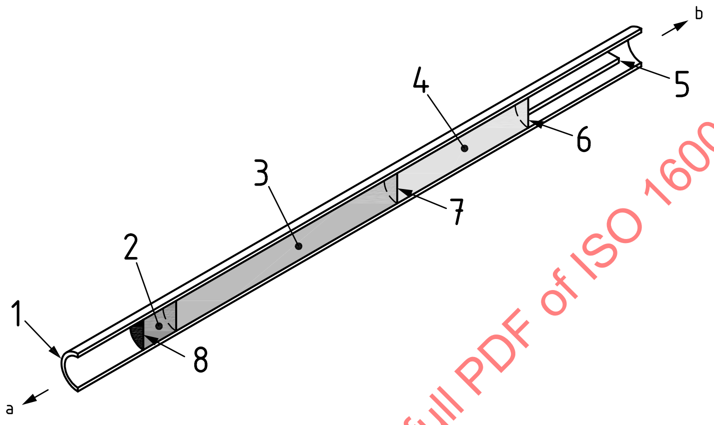
NOTE 3 Alternatively, even stronger sorbents are available (e.g. carbon molecular sieves) which allow ultra-volatile compounds such as C_3 hydrocarbons and vinyl chloride to be trapped. However, tubes packed with such very strong sorbents are prone to some water retention (see ISO 16017-1) and normally require an additional dry purge step prior to 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 A useful example sorbent combination comprises: quartz wool (5 mm); Tenax TA® (175 mg, ~35 mm); and 15–20 mm of Carbograph 5 TD® or Carbopack X® - suitable for compounds ranging in volatility from 1,3-butadiene to n-C_{30} or more depending on the capability of the thermal desorption instrument selected.

All sorbents shall 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 2).

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 2).



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 5 TD® 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 2 — Example of a metal tube packed with multiple sorbents for extending the target volatility range from 1,3 butadiene to n-C_{30}

NOTE 6 Optimum pump flow rates for multi-sorbent tubes of the dimensions described are in the range 20 ml/min to 200 ml/min.

NOTE 7 Inert-coated stainless steel or glass tubes are preferred for monitoring reactive, odorous compounds.

Sorbents with significantly different maximum temperatures should not normally be combined in a single tube or it can be difficult to completely condition one without overheating and degrading the other.

An alternative approach is to use tubes containing single sorbents of increasing strength connected together in series using inert unions (7.2) 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 pre-conditioned sorbent tubes are available commercially. Alternatively, sorbent tubes can be filled in the laboratory as specified in 7.1.1.

7.2 Sorbent tube unions

For sampling onto an assembly of two (or more) tubes in series. The sampling end of a secondary (back-up) tube can be connected to the non-sampling end of a primary sorbent tube using metal screw-couplings fitted with combined PTFE ferrules. Besides the metal screw couplings fitted with PTFE ferrules, fluorocarbon resin joints (unions) with Taper-Swaging Seal mechanism are also applicable to connecting sampling tubes. Two identical tubes can be connected in series – for example, as a check on the breakthrough of volatile compounds (9.1). Tubes containing different sorbents can also be connected in series (7.1.2).

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

7.4 Calibrated sampling system for pumping air through the sorbent tubes. Shall fulfil the requirements of EN 13137.

7.5 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 be used with inert tubing upstream of the sorbent. Interferences from the tubing can introduce contaminants.

7.6 Gas chromatographic system (GC), fitted with a mass spectrometer (optional FID) capable of detecting an injection of at least 1 ng of toluene with a signal-to-noise ratio of at least 5 to 1.

7.7 Capillary column. A GC capillary column of 5 % phenyl 95 % methyl polysiloxane phase is selected. Bonded 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. Simultaneous analysis of VVOC, VOC and SVOC requires more care with respect to column selection, it is dependent on the target list.

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

7.8.1 Types of thermal desorber

Two-stage thermal desorbers typically fall into two main categories depending on the type of secondary focusing device:

a) small, electrically-cooled sorbent traps desorbed in a reverse flow of carrier gas (i.e. with carrier gas flowing in the opposite direction to that used during focusing) and

b) focusing mechanisms which are desorbed with a forward flow of carrier gas (i.e. with the gas flowing in the same direction as that used during focusing).

7.8.2 General requirements

The following apply to all types of thermal desorption apparatus:

- Tube seals or 'analytical' caps shall be leak tight to protect sampled and desorbed tubes from analyte loss and contaminant ingress while they are on the analytical system. This is particularly critical for automated operation where tubes may be in situ for extended periods.
- When tubes are sealed into the carrier gas (sample) flow path ready for primary (tube) desorption, these seals shall be leak tested before desorption and without compromising the sample, to prevent analyte loss and misreporting.
- The mechanism for sealing tubes into the sample flow path shall also exclude artefacts from outer tube surfaces to prevent contamination.

- Air shall be pre-purged from the tubes to vent before primary (tube) desorption to prevent sorbent or analyte oxidation and to extend the life of the GC column and detector.
- Tubes shall be desorbed with carrier gas flowing in the reverse direction to the flow of air during sampling. This optimises the release of retained compounds and extends the volatility range of compounds which can be analysed simultaneously.
- Desorption conditions of temperature, time and carrier gas flow rate shall be adjustable.
- The rate of compound release from the focussing device during secondary (trap) desorption shall be sufficiently fast for compatibility with high resolution capillary chromatography.
- The two-stage desorption process shall enable quantitative splitting of the sample during secondary desorption to extend the compatible concentration range.

NOTE 1 Some apparatus also incorporates additional features such as automatic sample-tube loading, the addition of gas-phase internal standard onto the sampling end of tubes (or focusing traps) immediately before each tube is desorbed, dry purging of tubes (in the sampling direction) before primary desorption, sample splitting during primary (tube) desorption and quantitative re-collection of sample split flow for repeat analysis and validation of compound recovery.

NOTE 2 The addition of gas phase internal standard onto the sampling end of sorbent tubes (or onto the focusing trap) immediately before primary (tube) desorption, provides a valuable check on the integrity of the analytical caps (or other means of sealing tubes) while tubes are awaiting desorption during automated operation. It allows users to distinguish between detector drift and analyte loss if there is any apparent loss of signal during a sequence (see 10.1.1.2).

Tube dry purging can be required prior to desorption if sample tubes containing very strong (water retentive) sorbents (see Note 3 of 7.1.2) have been used to sample humid air. This minimises analytical interference and measurement uncertainty.

7.9 Injection facility

The injection facility is required if standard tubes are being prepared by liquid spiking (optional). A conventional gas chromatographic injection unit or equivalent device may be used for preparing calibration standard tubes. 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.

7.10 Mass spectrometer, for identification of target compounds and investigation of unknowns. It is also used for quantification.

NOTE Optional Flame ionisation detector (FID): While the retention time of a GC peak using FID cannot, on its own, be used as confirmation of compound identity, it increases confidence in peak identification (assignment) by GCMS, if the peak retention time also corresponds to that of the respective standard on FID.

FID responses are typically stable and linear over many orders of magnitude making them suitable for quantification. However using FID in conjunction with MS in dual detector format, may compromise the sensitivity of the method. It is also difficult to accurately quantify unresolved (overlapping) chromatographic peaks using FID alone.

8 Conditioning and storage of sorbent tubes

8.1 Conditioning

Prior to each sampling use, condition the pre-cleaned sorbent tubes using more stringent conditions than those required for analysis (temperatures and flows), but taking care not to exceed the maximum temperature of the least stable sorbent in the tube. Analyse a representative number of conditioned tubes using routine analytical parameters, to ensure that the thermal desorption blank is sufficiently small. The sorbent tube blank level is acceptable if interfering artefact peaks do not exceed 2 ng for each of the target analytes. If the method requires summation of VOC or SVOC (TVOC or TSVOC – see Annex A) then any TVOC or TSVOC levels in the blank should not exceed 20 ng. 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 re-packed or replaced (see procedure in 7.1.1).

Do not exceed the maximum temperature of the sorbent during tube conditioning or analysis.

NOTE Generation of benzaldehyde and acetophenone from Tenax TA® might be increased by ozone in the sampling air.

8.2 Storage of conditioned sorbent tubes before sampling

Seal conditioned sorbent tubes with metal screw-cap fittings with combined PTFE ferrules and store in a sealed container at room temperature. The container shall be clean and low emission such that the levels of artefacts introduced onto sealed tubes during storage does not cause them to exceed the requirements of 8.1. Use conditioned sampling tubes within four weeks. Recondition tubes stored for more than four weeks before sampling.

One or two of the conditioned tubes from the batch selected for each sampling exercise shall be retained as laboratory blank tubes (3.8). These are noted. They shall be analysed with the sampled tubes and shown to meet the performance specification detailed in 8.1.

9 Sampling

9.1 Air sampling

If more than one sorbent tube is being used as a check on analyte breakthrough, prepare a tube assembly by joining two identical tubes in series with a union (7.2). Connect the sampling end of the sorbent tube or tube assembly to the sampling line (if applicable) and attach the pump to the non-sampling end of the sorbent tube or tube assembly using low emission tubing (7.5). Start the pump and note and record the sampling flow rate, starting time, temperature and, if necessary, for calculation, also atmospheric pressure. An appropriate sampling flow rate for the broadest volatility range of vapour-phase organic compounds is in the range of 20 ml/min to 200 ml/min. At the end of the sampling period, note and record the flow rate, turn the pump off, and note and record the time, temperature and, if necessary, atmospheric pressure. Disconnect the sampling tube or tube assembly from the sampling line and seal both ends using screw-cap fittings with PTFE ferrules.

In order to minimize risk of condensation when sampling humid environments, the temperature of the sorbent tube should not be lower than the sampled air.

NOTE Depending on circumstances it can be useful to record relative humidity.

9.2 Sampling volumes

Safe sampling volumes (SSV), i.e. amounts of gas that can be sampled without breakthrough of possible target compounds, are listed in Annex E. Typical sampling volumes when sampling VOCs from non-industrial indoor air are 3 l to 20 l. In material emission measurements, the material type and age, loading factor and air exchange rate in the chamber determine suitable sampling volumes. Sampling volumes should be adjusted to concentration range, boiling point of target compounds and sorbents.

NOTE 1 For a broader study on using sorbent tubes and TD-GC-MS for the analysis of a range of semi-volatiles, including polycyclic aromatic hydrocarbons, polychlorinated biphenyls (PCB), phthalate esters and certain pesticides, see[22].

NOTE 2 When using Tenax TA® as a single sorbent a maximum sampling volume of 5 l is widely applied to prevent breakthrough of benzene on Tenax TA®.

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

9.3 Storage of loaded samples

To avoid possible changes, the sample should be analysed as soon as possible and preferably within four weeks after collection and with validated calibration. Loaded sampling tubes shall be tightly sealed using the caps described in 8.2 and stored in a low emission container at ambient room temperature (single sorbents) or under refrigerated conditions (multi-sorbent tubes).

NOTE 1 The effect of storage on loaded VVOC, VOC and SVOC from indoor or chamber air is not known for every sorbent and compound combination, although some data suggests that VOC may be stable over several months at room temperature (see ISO 16017[23],[24],[11],).

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 re-equilibrate with room temperature before they are opened for analysis.

NOTE 2 Information on recovery of VOC from sorbent tubes after storage is given in Annex F and in ISO 16017-1.

In the case of long-term emission chamber tests, it is possible to store the sampling tubes and measure all tubes with one calibration. However, certain substance groups (e.g. aldehydes, monoterpenes and thiols) may start to degrade on the sorbent within a few days. In such case the analysis for the loaded tubes should be performed in a timely manner.

9.4 Field blanks

Field blanks (3.9) 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 undertaken and analysed as part of each study.

10 Analysis

10.1 Determination of VOC, VVOC and SVOC

10.1.1 Analytical System

10.1.1.1 Checks on analytical system performance

Routine system calibration processes (multi- and single-level) allow analytical performance to be evaluated in respect of sample tube integrity, dynamic range, linearity, repeatability and sensitivity. Relevant performance criteria are listed below.

Analyte recovery through the two-stage thermal desorption process is validated by repeating the multi-level TD-GC-MS (and/or optional FID) calibration procedure using liquid injection and comparing the two curves (see ISO 16017-1 and other methods). An alternative method is e.g. to load the sorbent with the highest calibration level and desorb the tube twice. The second desorption should show analyte concentration less than 5 % of the first desorption. Alternatively, thermal desorbers allow quantitative re-collection of the split portion of TD samples, either pre or post column. In this case, subsequent analysis of the re-collected sample allows simple identification of any compounds with lower recovery than expected – i.e. proportionally lower than other compounds in the standard and/or lower than that predicted from the split ratio.

NOTE 1 Poor recovery of compounds through the thermal desorption process might be due to incomplete desorption or to condensation or degradation within the system flow path.

Other chromatographic performance criteria shall be evaluated using a suitable 'reference standard' prepared using a check material. This shall be used when the method is first set up, whenever there is a modification to the system and at least once a quarter (every three months) or with higher frequency if analytically required. It shall also be used whenever routine GC data from samples or standards indicates that system performance is deteriorating. A 'check material' is a chromatographic test mix containing analytes that are representative of the range of compounds of interest.

NOTE 2 An example check material is described in EN 16516.

Records of routine chromatographic checks using this reference standard shall be maintained for each analytical system (detailed in 10.1.1.2, 10.1.1.4, 10.1.3 and Clause 14).

10.1.1.2 Analytical system performance criteria

The following analytical system performance criteria shall be demonstrated:

a) sensitivity of the apparatus: this should meet the requirements set for quantification (see 10.1.4);

b) Chromatographic resolution: this shall be sufficient to allow the analytes to be separately quantified. This may be demonstrated if the resolution is sufficient to separate cyclohexanone and o-xylene; e.g. as described in Figure 3 at least to the extent that the two apexes (tops of the peaks) can be observed.

If using hydrogen carrier gas all relevant safety precautions should be adhered to.

NOTE 1 Other indicators for good chromatographic resolution are achieving separation between methyl methacrylate (CAS 80-62-6) and methyl cyclohexane (CAS 108-87-2) or butylhydroxyltoluene (CAS 128-37-0) and dodecanoic acid methyl ester (CAS 111-82-0).

NOTE 2 Deterioration of the shape of the phenol peak (e.g. increased tailing) is another good indicator of the deterioration of the analytical system performance.

NOTE 3 If appropriate quality helium (or hydrogen) carrier gas is used (minimum 99,999 % pure), ideally with an oxygen trap fitted, it is usually possible to maintain TD-GC-MS system chromatographic performance between routine annual maintenance visits, depending on sample throughput. However, if chromatographic performance deteriorates and these critiera cannot be met, consider checking the status of:

- all connections in the sample flow path;
- the thermal desorption focusing trap;
- the GC capillary column.

The focusing trap may need repacking or replacing. The first 30 cm of the column may need to be removed or the capillary column may need replacing.

c) Linearity: The linear regression coefficient should be above 0,99 for toluene across the calibration range.

d) System and sample stability during batch analysis: Mid-range single level standards shall be interspersed between samples at a frequency of e.g. one standard every 10 samples. If the analytical TD-GC-MS process is being automated, the standard tubes shall be loaded onto the system at the same time as the samples. The response of the standards shall be monitored to check for loss of signal over the duration of the sequence. All compounds in repeated single level calibrations should meet the performance criteria given in 10.1.3 and Clause 14.

NOTE 4 Loss of signal, if it does occur can be the result of detector drift or loss of analyte caused by inadequate sealing with tubes awaiting desorption (e.g. on an autosampler). The stability of data from gas phase internal standards introduced immediately prior to the desorption of each tube (see Note 2 of 7.8.2) can be compared to the stability of results from the series of mid-range-single-level standards run with each batch of samples in order to distinguish the cause of any drift – be it changing detector response or loss of analyte from tubes waiting for automatic analysis.

e) Long-term system stability: this should be checked by plotting a control chart with the response of all the compounds in the check material every time it is analysed. The control chart of each analytical system should be kept until the instrument is decommissioned. An acceptance limit of two times the standard deviation shall be applied along with the following assessment criteria:

  o if one control measurement is outside ± 3 standard deviations this means that the acceptance criterion is exceeded;

  o if the second consecutive measurement is on the same side outside ± 2 standard deviations, this means that the acceptance criterion is exceeded.

f) Dynamic range: It shall be possible to quantify peaks at levels which are at least 100 times above their respective lower limit of quantification.

g) Repeatability: Sample and standard repeatability requirements are detailed in Clause 14.

10.1.1.3 Tune requirements for the mass spectrometer

The mass range scanned is typically 29 amu to 550 amu. The mass spectrometer should be tuned whenever the vacuum has been broken (e.g. to change the column or to install or clean the source). The tune needs to be repeated if the quality of mass spectral matches for compounds in the calibration standard or check material begin to deteriorate.

NOTE When scanning from 29 amu, interference from O_2 and N_2 from leakage might occur in the mass spectrum. This might disturb matching with the mass spectra library and would result in a lower spectral match.

10.1.1.4 Laboratory proficiency testing schemes and participation in round-robin exercises

Relevant laboratory proficiency testing (PT) schemes are available and participation is strongly recommended. In this case thermal desorption tubes pre-loaded with relevant target components are distributed for evaluation and reporting by participating laboratories. Participation in material emission and indoor air testing round-robin exercises is also strongly recommended. In this case, either suitable (homogenous and stable) example construction products or in case of indoor air, tubes used by the reference laboratory to sample a given atmosphere, are typically distributed for evaluation and reporting by participating laboratories.

10.1.2 Identification of target compounds

Chromatographic peaks shall be identified by retention time and comparison with spectra obtained from standards or from commercial libraries. The identification of a compound is confirmed if a reliable spectral match is made (typically equal or better than 80 %) and if the retention times match. A lower match quality can be used for identification only if there is additional, independent evidence to confirm compound identity (for example, the presence of known isomers, typical contaminants, typical emission profiles of similar products, presence of the compound at another testing time). Otherwise the substance shall be marked as not identified.

If hydrogen is used as carrier gas, analytical conditions may need to be adjusted for optimum performance and calibration, and all QC tests must be performed with hydrogen carrier gas.[30] Note that guidance should be taken from the GC/MS manufacturer to determine if any other aspects of library matching need to be considered.

NOTE The choice of baseline substraction method, spectral deconvolution approach, library search algorithm, spectral database and mass spectral tuning criteria are all factors in obtaining a reliable compound match.

10.1.3 Quantification of target compounds and compounds according to task list

For quantification by MS, chromatographic peaks shall be integrated using quantifier and qualifier mass ions extracted from the TIC signal. The choice of quantifier and qualifier ions for each compound shall be documented and available in the laboratory and shall be reported if requested. Where possible, quantifier and qualifier ions shall be selected that are not present in neighbouring peaks and that are major fragments of the compound in question. Using the total ion signal of the mass spectrometer is a poor estimate of the integrated mass.

NOTE 1 Using extracted ions for quantification improves selectivity and signal to noise ratios.

Extracted ion data, including sub-unit mass data (where available), shall be used to resolve co-eluting peaks or clusters of peaks and identify/quantify individual compounds as accurately as possible.

NOTE 2 Alternatively, if spectral deconvolution software is available, it can be used to define, identify and quantify individual compounds in both co-eluting peaks and peaks which appear as unresolved clusters in the TIC.

If co-eluting peaks remain unresolved, all major components shall be identified and the entire affected chromatographic area quantified by dropping perpendiculars to baseline in the valleys between the major components (Figure 3). For interpretation and quantification of complex chromatograms that show clusters of peaks that cannot be resolved, these clusters should not be separated into solitary peaks, but the total area of the whole agglomerate should be calculated and quantified using the most appropriate authentic response factor (for a group of target compounds) or the TIC response factor for toluene. Typical clusters could originate from technical mixtures such as hydrocarbons or glycols (Figure 4). Clusters that span over hexadecane (as VOC/SVOC-border) shall be split into a VOC- and an SVOC-part with a perpendicular to the baseline at the retention time of n-hexadecane.

During initial system set-up, the analytical system shall be quantified using a minimum five-point multi-level calibration over a range of at least 20 (i.e. the factor between the lowest and highest mass in the range shall be at least 20). Data from this initial calibration phase should be used to determine a relative response factor (RRF) for each compound of interest, relative to an internal standard such as toluene D8. At least one appropriate (e.g. mid-level) standard, containing toluene and the expected target compounds (or at least a set of compounds that is representative of the volatility and polarity range of the relevant target compounds), shall be run at the start of each batch of samples and be interspersed with the sample tubes – e.g. every 10th sample – as a check on relative response factor stability. The multi-level calibration for one or more specific compounds of interest shall be repeated whenever the single level calibration for that type of compound shows unacceptable drift in actual or relative response factors since the previous multi-level calibration. See also 14.

NOTE 3 The set of compounds that is representative of the volatility and polarity range of target compounds could be the same as those contained in the check material.

NOTE 4 Use of an internal standard (e.g. toluene D8 or cyclodecane) can be used to ensure accuracy and as a further check on analytical system stability.

Identified target compounds shall be quantified using the actual response factor for each compound. Identified non-target compounds shall be quantified using the TIC relative response factor for toluene (i.e. in ‘toluene equivalents’).

NOTE 5 Additional use of the actual response factors for quantifying identified non-target compounds can provide useful supplemental information.

NOTE 6 Determining VOC using 'toluene equivalents' is necessary for non-identified compounds (and for non-target compounds under some test protocols). This determination is semiquantitative since the individual compounds in the mixture may have actual response factors which differ widely from the toluene response factor.

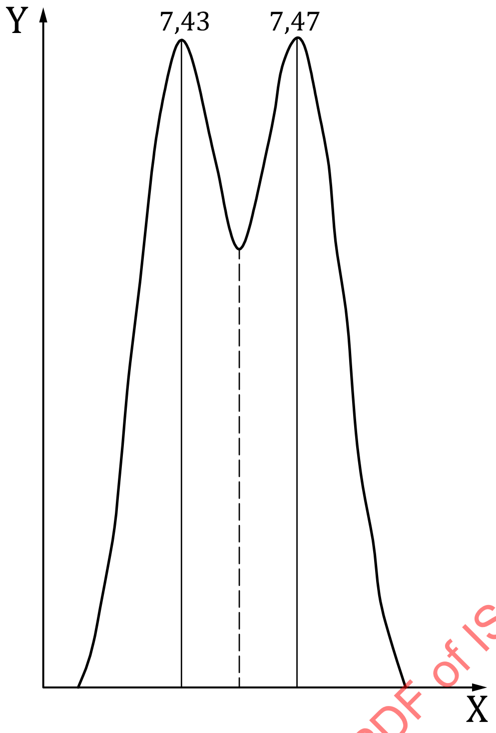


Figure 3 — Depiction of a suitable integration method for chromatographical compounds which do not fully resolve

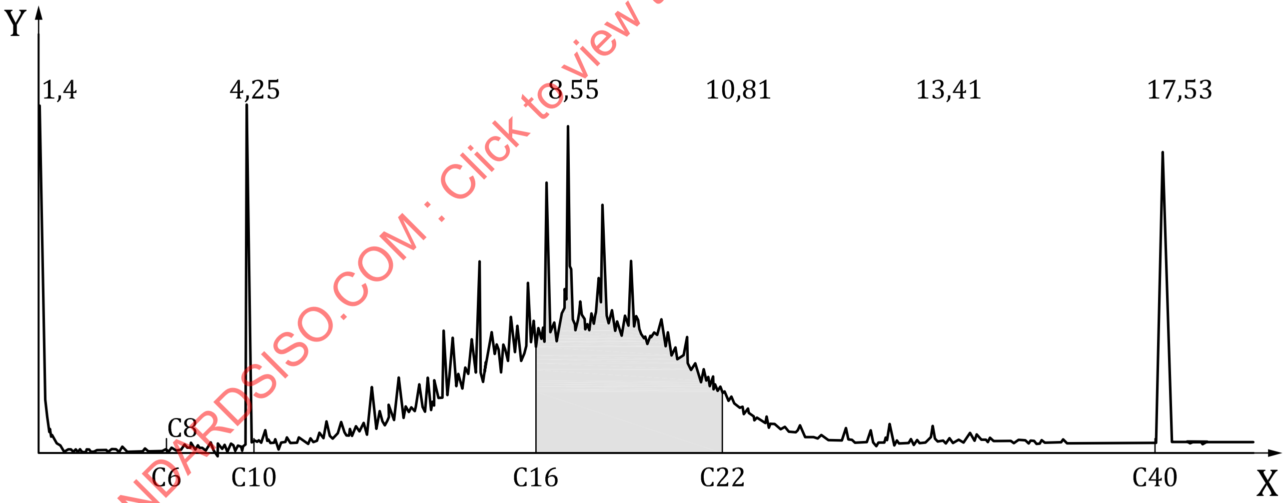


Figure 4 — Depiction of a suitable integration method for complex mixtures of chemical homologues which do not fully resolve

NOTE 7 For quantification by FID such as the reporting of $TVOC_{FID}$ (see Annex A) then the quantification procedure should follow a similar procedure to that described in 10.1.3 but applying the respective FID response factor for each individual compound. $TVOC_{FID}$ concentrations can also be calculated by applying the FID response factor for toluene to the entire peak area eluting between n-hexane to n-hexadecane inclusively.

10.1.4 Determining the lower limit of quantification

The quantification limit is defined as equal to 10 times the standard deviation of the results for a series of at least 12 replicate tubes spiked with the compounds of interest from the check material at levels at or near the quantification limit. The quantification limit shall be below 5 ng for the compounds in the check material except phenol. A limit of 5 ng on tube is equivalent to 1 µg/m^3 in the sampled air, assuming a 5 l air sample volume. The quantification limit for phenol shall be below 25 ng which is equivalent to 5 µg/m^3 in the sampled air assuming a 5 l air sample volume. For the relevant carcinogenic compounds (see EN 16516[13]), the quantification limit shall be below 5 ng on tube or 1 µg/m^3 (assuming a 5 l air sample volume) in the air as far as feasible. The actual quantification limit for any compound which fails these criteria shall be reported.

If any check material compounds fail to meet these quantification limits, consider possible causes.

The quantification limit of any target vapour-phase organic compounds shall be 1 µg/m^3 if feasible or as low as possible.

10.2 Identified non-target compounds and unidentified compounds

Those compounds not listed in the target list shall be identified by mass spectra, if required.

For identification and quantification of single, non-target and unidentified VOC, analyse the samples with MS operating in the scan mode. Identify single compounds 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 on its own be regarded as proof of identity.

Identify as many compounds as possible according to the task. Commonly reported are those representing the 10 highest peaks and those present at concentrations above 2 µg/m^3, quantified as toluene equivalent. A list of VOC which, according to experience at the time of publication, are frequently encountered in indoor air and emitted from materials is given in Annex B. A satisfactory level of identification has been achieved if the chromatographic peak areas of identified VOC when summed correspond to at least two-thirds of the total area of all the peaks in the chromatogram.

For quantification of identified non-target compounds a chemically similar component can be used, if available. Unidentified compounds should be quantified as toluene equivalent.

11 Concentration of analytes in the sampled air

The peak area of each individual organic compound is 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 by Formula (1). The slope of the calibration curve over the linear range is the response factor of the compound studied.

$$A_{St} = b_{St} * m_{St} + c_{St} \qquad (1)$$

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 the analyte in the standard;

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

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 given in Formula (2):

$$m_A = \frac{A_A - c_{St}}{b_{St}} \tag{2}$$

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

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

$$\rho_A = \frac{m_A - m_{A0}}{V} \tag{3}$$

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 volumes are converted to other temperatures and pressures (reference conditions).

If necessary, the concentrations are adjusted to other temperatures x and 101,3 kPa see Formula (4):

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

where

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

t is the actual temperature, in Kelvin, of the air sampled.

NOTE Concentrations resulting from the conversion of the sampling volume do not reflect the concentration at real test conditions or concentrations resulting at the reference conditions.

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) volume

   2) temperature

   3) 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

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 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 butadiene's 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 %[26].

The repeatability of sampling of non-polar hydrocarbons from cylinder atmospheres containing six VOCs has been reported. For 2 l samples, the repeatability for Tenex TA® was less than 10 %, and for 0,5 l samples it was 12 %[16].

NOTE In material emission testing, interlaboratory comparisons have been organized to assess the agreement between laboratories undertaking tests to characterize the emissions from VOC from indoor materials and products. The results of these intercomparison have been published[17],[18].

13 Test report

The test report shall contain at least the following information:

- a) list of measurement tasks;
- b) description of the sampling location, if the task requires it;
- c) time and date of the sampling;
- d) sampling conditions (temperature, relative humidity; atmospheric pressure);

e) reference to this document (i.e. ISO 16000-6);

f) full description of the sampling procedure;

g) full description of the analytical procedure;

h) quantification limits of the analytical method;

i) field blanks shall be reported, if the task requires it;

j) concentrations of identified compounds (target compounds and target sum parameters), provided with CAS numbers, and non-identified compounds including calculation and calibration principles used;

k) uncertainty of the reported results.

NOTE Typically test results are reported with not more than two significant figures if below 10 µg/m^3, report only one significant figure. This rule reflects the degree of precision that can be achieved by this testing method. Examples:

— 4,5 and 5,4 both are expressed as 5;

— 52,5 and 53,4 both are expressed as 53;

— 255,0 and 264,9 both are expressed as 260;

— 2550 and 2649 both are expressed as 2600.

14 Quality control

An appropriate level of quality control shall be employed and documented. See also 10.1. Important checks include:

a) Single level standards interspersed with a batch of samples (10.1.1.1). These shall be compared with each other and with the most recent multi-level calibration (10.1.3). Single level standard results should not deviate more than ± 15 % of their mean and not more than ± 15 % of the values given by the most recent multi-level calibration for at least 90 % of compounds. If unacceptable, a new multi-level calibration shall be undertaken.

b) Each sampling exercise shall include at least one duplicate sampling event (9.1). The compound concentration determined from duplicate air samples should not deviate more than ± 15 % of their mean, after taking the air sample volume into account. If there is any greater disparity, only the higher concentration shall be reported unless there is a good technical reason (e.g. artefact or contamination) why the higher value should be discounted. This should be documented.

c) Notified and accredited laboratories should verify the performance of the whole method by participating in relevant proficiency testing schemes and round-robin exercises, by using certified reference materials and samples as regularly as possible and by following the quality control requirements of ISO 16000-9:2006 and ISO 16000-11:2006 (see 10.1.1.4).

d) Field blanks are prepared in accordance with 9.4. Background levels are acceptable if levels of target compounds or interfering artefacts do not exceed 2 ng.

e) Desorption efficiency (10.1.1.1) shall be better than 95 % for all reported compounds.

f) Sample collection efficiency shall be determined by using back-up tubes or taking samples of different sampling volumes in parallel (9.1). Breakthrough levels are satisfactory if subsequent analysis of the back-up tube shows less than 5 % of any compound of interest, compared to the primary tube.

Annex A
(informative)

Total volatile organic compounds (TVOC) and total semi-volatile organic compounds (TSVOC)

A.1 Total volatile organic compounds (TVOC)

A TVOC measurement comprises the concentration (mass per unit air volume) of identified and unidentified volatile organic compounds, as defined in 3.4.

There are three ways of determining the TVOC, which lead to three different versions of the TVOC parameter:

1) **Calculation of TVOC based on TIC/FID ($TVOC_{TIC/FID}$):** The concentration determined from the sum of all compounds masses eluting in a defined section of the chromatogram, quantified using either the FID response factor for toluene or the TIC response factor for toluene, after correcting for blank values of the respective compounds quantified in the same way.

2) **Calculation of TVOC based on identified and not identified compounds ($TVOC_{ID}$):** The concentration determined from the sum of all identified target compounds (see 3.6) (quantified using authentic standards) plus all identified non-target compounds and non-identified compounds (quantified using the TIC response factor for toluene) eluting in a defined section of the chromatogram, after correcting for blank values of the respective compounds quantified in the same way. This option could be argued to provide a value that most closely represents the actual total concentration of VOC emitted under the test conditions, but requires a harmonized list of target compounds for consistent results.

3) **Calculation of TVOC based on the sum of integrated peaks quantified as toluene equivalents ($TVOC_{MEQ}$):** The concentration determined from the VOC mass derived from the total area of a defined section of the chromatogram, obtained using a specific column, calculated using the TIC or FID response factor for toluene after substracting the total area of the same section of the equivalent chromatogram.

CAUTION — These parameters all give different values and cannot be used interchangeably.

A.2 Total semi-volatile organic compounds (TSVOC)

A TSVOC measurement (if required) comprises the sum of the concentration of the identified and unidentified semi-volatile organic compounds, as defined in 3.1 and the respective task list. Like the TVOC value, it can be determined in several ways (see A.1).

NOTE For example EN 16516 limits the TSVOC range to n-hexadecane to n-docosane(n-C_{22}).

A.3 Limitations of TVOC and TSVOC values

TVOC and TSVOC values are sum parameters and different calculation methods are used as stated above. TVOC and TSVOC values are also dependent on the choice of sorbents in the sampling tube, sorbents in the focussing trap, and the detector type and will vary from FID to MS and between different types of MS. Therefore, the results can be compared between FID and MS only when using results obtained with compound specific standards.

TVOC and TSVOC emission values comprise an undefined mix of compounds of varying or poorly defined toxicity. They are not reliable indicators of the impact of product emissions or indoor air quality with respect to human health.

Annex B
(informative)

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

Table B.1 — Examples of compounds detected in indoor air and emitted from building products in test chambers[17],[18]

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	185
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
Aliphatic hydrocarbons *n*-C_6 to *n*-C_{16}		
1-Decene	872-05-9	171
1-Octene	111-66-0	121

Table B.1 *(continued)*

Chemical compound	CAS No.	Boiling point °C
2,2,4,6,6-Pentamethylheptane	13475-82-6	178
2,4,6-Trimethyloctane	62016-37-9	172
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
Terpenes		
ß-Caryophyllene	87-44-5	275
α-Pinene	80-56-8	156
ß-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

Table B.1 *(continued)*

Chemical compound	CAS No.	Boiling point °C
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-*tert*-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
Aldehydes		
2-Butenal	123-73-9	104
2-Decenal	2497-25-8	78 to 80
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	244 to 245
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]

Table B.1 *(continued)*

Chemical compound	CAS No.	Boiling point °C
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
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

Table B.1 *(continued)*

Chemical compound	CAS No.	Boiling point °C
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
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 E.

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

NOTE 3 For some compounds the boiling points are not known.

[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 C
(informative)

Description of sorbents

Table C.1 — List of sorbents

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
Sherocarb	Carbon molecular sieve
Tenax TA	Poly(diphenyl oxide)
Tenax GR	Graphitized poly (diphenyl oxide)

NOTE All sorbents given here are trademarks of different manufactures. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the products named. Equivalent products may be used if they can be shown to lead to the same results.

Annex D
(informative)

Guide on sorbent usage

Tubes containing Tenax TA® can generate low levels of benzene artefacts over time, even if the tube was shown to be free of benzene immediately after conditioning. False-positive results may impair the determination in the low µg/m^3 range of benzene. It is therefore recommended to verify any such low benzene values with an independent second test using sorbent tubes packed with alternative sorbents such as carbon blacks (see EN 14662-1[12]).

Table D.1 — Sorbent usage

Type	Sorbent	Analyte range	Conditioning at max. (°C)	Desorption max. (°C)	Hydrophobic	Notes
Polydimethyl-siloxane PDMS	3 % OV-101	Semi-volatiles – compounds less volatile than n-C_{16}				working on gas-liquid chromatographic principles, this adsorbent is more commonly used as a GC stationary phase, but has been found suitable for very high boiling air pollutants
	10 % OV-101					
	Various suppliers					
very weak graphitized carbon black	Carbopack C	n-C_8 to n-C_{20}	400	360	Yes	artefacts per tube: individual VOC < 1 ng, friable, recommended mesh size: 40/60, some activity for labile compounds, desorption efficiency: medium, (some band broadening), typical surface area: 10 m^2/g
	Carbotrap C		400	360	Yes	
	Carbograph 2 TD		400	360	Yes	
	Anasorb GCB 1		400	360	Yes	
	Carbopack F		400	360	Yes	
	Carbotrap F		400	360	Yes	
	Carbopack Y		400	360	Yes	
	Carbotrap Y		400	360	Yes	
Weak porous polymer	Tenax TA™	n-C_6 to n-C_{22}	320	280	Yes	artefacts per tube: 1-2 ng of some VOC (incl. benzene). very inert; desorption efficiency good (narrow peaks); typical surface area: 30 m^2/g; recommended mesh size: 35/60
	Tenax GBR		320	280	Yes	
Weak to medium graphitized carbon black	Carbopack B	n-C_5 to n-C_{14}	400	360	Yes	
	Carbotrap		400	360	Yes	
	Carbograph 1 TD		400	360	Yes	
	Carbograph 4 TD		400	360	Yes	
	Anasorb GCB2		400	360	Yes	

Table D.1 *(continued)*

Type	Sorbent	Analyte range	Conditioning at max. (°C)	Desorption max. (°C)	Hydrophobic	Notes
Various medium strength porous polymer sorbents	Chromosorb Century series	Varies within range n-C_5 to n-C_{14}. Some of these sorbents are very specific for a given polarity or compound group			Yes	low desorption temperatures (range: 180-200 °C) – preclude use in multi-bed tubes; hydrophobic artefacts per tube: individual VOC< 10ng; use of these sorbents is reducing due to supply issues, high background and high batch-to-batch variability.
	102			180-200	Yes	
	106 Porapaks			180-200	Yes	
	Porapak Q			180-200	Yes	
	Porapak N			180-200	Yes	
Medium to strong graphitized carbon black	Carbopack X	1,4-butadiene to benzene	400	360	Yes	artefacts < 1 ng, friable; recommended mesh size 40/60; some activity for labile compounds, desorption efficiency poor (band broadening), typical surface area: 240 m^2/g
	Carbograph 5 TD		400	360	Yes	
	Carbograph 4 TD		400	360	Yes	
Carbon molecular sieve	Carboxen 1003	n-$C_{2/3}$ to n-$C_{5/6}$	350	330	No	artefacts < 1ng per tube; recommended mesh size: 40/60; desorption efficiency poor (band broadening); typical surface area: 400-1000 m^2/g, retention volumes reduced significantly when > 80 % RH
	Carboxen 569		350	330	No	
	Sulficarb (formerly Unicarb or Spherocarb)		350	330	No	
	Carbosieve SIII		350	330	No	
	Anasorb CMS		350	330	No	
	Carboxen 1000		350	330	No	
	Carboxen 56		350	330	No	
Others	Quartz wool	$\sim C_{30}$	Na	na	Yes	
	Glass wool		Na	Na	Yes	
	Glass beads		na	Na	Yes	