PD CEN/TS 13649:2014

BSI Standards Publication

Stationary source emissions — Determination of the mass concentration of individual gaseous organic compounds — Sorptive sampling method followed by solvent extraction or thermal desorption

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National foreword

This Published Document is the UK implementation of CEN/TS 13649:2014. It supersedes BS EN 13649:2002 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee EH/2/1, Stationary source emission.

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

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

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English Version

Stationary source emissions - Determination of the mass concentration of individual gaseous organic compounds - Sorptive sampling method followed by solvent extraction or thermal desorption

Emissions de sources fixes - Détermination de la concentration massique en composés organiques gazeux individuels - Échantillonnage par adsorption et extraction par solvant ou thermodésorption

Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von gasförmigen organischen Einzelverbindungen - Sorptive Probenahme und Lösemittelextraktion oder thermische Desorption

This Technical Specification (CEN/TS) was approved by CEN on 25 August 2014 for provisional application.

The period of validity of this CEN/TS is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the CEN/TS can be converted into a European Standard.

CEN members are required to announce the existence of this CEN/TS in the same way as for an EN and to make the CEN/TS available promptly at national level in an appropriate form. It is permissible to keep conflicting national standards in force (in parallel to the CEN/TS) until the final decision about the possible conversion of the CEN/TS into an EN is reached.

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Foreword

This document (CEN/TS 13649:2014) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

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

This document supersedes EN 13649:2001.

Significant technical changes between this Technical Specification and the previous edition of EN 13649 are:

a) the status of the document has been changed from European Standard (EN) to Technical Specification (TS);

b) the scope has been clarified regarding the use of the TS and its applicability;

c) a decision tree for the determination of the sampling procedure has been included;

d) the sampling strategy has been aligned with EN 15259;

e) the thermal desorption technique has been added;

f) comprehensive information on the validation of monitoring methods for speciated organic substances in stack gas is given.

According to the CEN-CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this Technical Specification: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

1 Scope

This Technical Specification specifies procedures for the sampling, preparation and analysis of individual volatile organic compounds (VOCs) in waste gas, such as those arising from solvent using processes. Sampling occurs by adsorption on sorbents, preparation by solvent extraction or thermodesorption and analysis by gas chromatography.

Examples of individual VOC are given in relevant industry sector BAT Reference documents (BREFs).

The results obtained are expressed as the mass concentration (mg/m^3) of the individual gaseous organic compounds. This document is suitable for measuring individual VOCs whose ranges vary depending on compound and test method, refer to Annex B and C.

This Technical Specification may be used to meet the monitoring requirements of the Industrial Emission Directive (IED) and associated supporting documents.

This Technical Specification is not suitable for measuring total organic carbon (TOC). For the measurement of the mass concentration of total organic carbon then EN 12619 [3] is applicable.

2 Normative references

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

EN 15259, *Air quality - Measurement of stationary source emissions - Requirements for measurement sections and sites and for the measurement objective, plan and report*

EN ISO 14956, *Air quality - Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty (ISO 14956)*

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

3 Terms and definitions

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

3.1
desorption efficiency
ratio of the mass of the recovered organic material to the mass of organic material collected by the adsorbent expressed as a percentage

3.2
sampling tube for solvent extraction
glass tube filled with activated carbon as the adsorbent

3.3
sampling tubes for thermal desorption
stainless steel, inert-coated steel or glass tube-form samplers supplied capped and packed with one or more conditioned, thermal desorption compatible sorbents

3.4
uncertainty
parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand

[SOURCE: ISO/IEC Guide 98-3:2008 [2]]

3.5
volatile organic compound
VOC
any organic compound having at 293,15 K a vapour pressure of 0,01 kPa or more, or having a corresponding volatility under the particular conditions of use

3.6
field blank
value determined by a specific procedure used to ensure that no significant contamination has occurred during all steps of the measurement and to check that the operator can achieve a quantification level adapted to the task

4 Principle

There are three steps in the measurement of individual gaseous organic compounds: sampling, desorption and analysis.

Sampling approaches vary depending on waste gas conditions. Suitable sorbent shall be selected. This document specifies solvent extraction or thermal desorption. Analysis is by gas chromatography.

Other methods may also be applicable e.g. canister, as an alternative to sorbent sampling for very volatile compounds, or condensate trap (catchpot) sampling systems, as an alternative to dilution sampling, providing their suitability can be demonstrated, e.g. according to CEN/TS 14793 [1].

Figure 1 shows the decision tree for determining the sampling procedure.

5 Apparatus and materials

5.1 Method of measurement

The sample gas is extracted from the waste gas exhaust duct via a sampling system and onto a solid sorbent tube using a pump. The solid sorbent tube is then solvent extracted or thermally desorbed and the compounds are determined by gas chromatography.

Many of the solvent using processes covered by the Industrial Emissions Directive produce waste gases which do not have a high water content. This document requires the use of a dilution sampling system when the concentration of water or solvent is high enough to cause the risk of condensation.

NOTE The limit values of EU Directives are expressed in mg/m^3, on a wet basis, for non-combustion process and on a dry basis, for combustion processes, at the reference conditions of 273 K and 101,3 kPa.

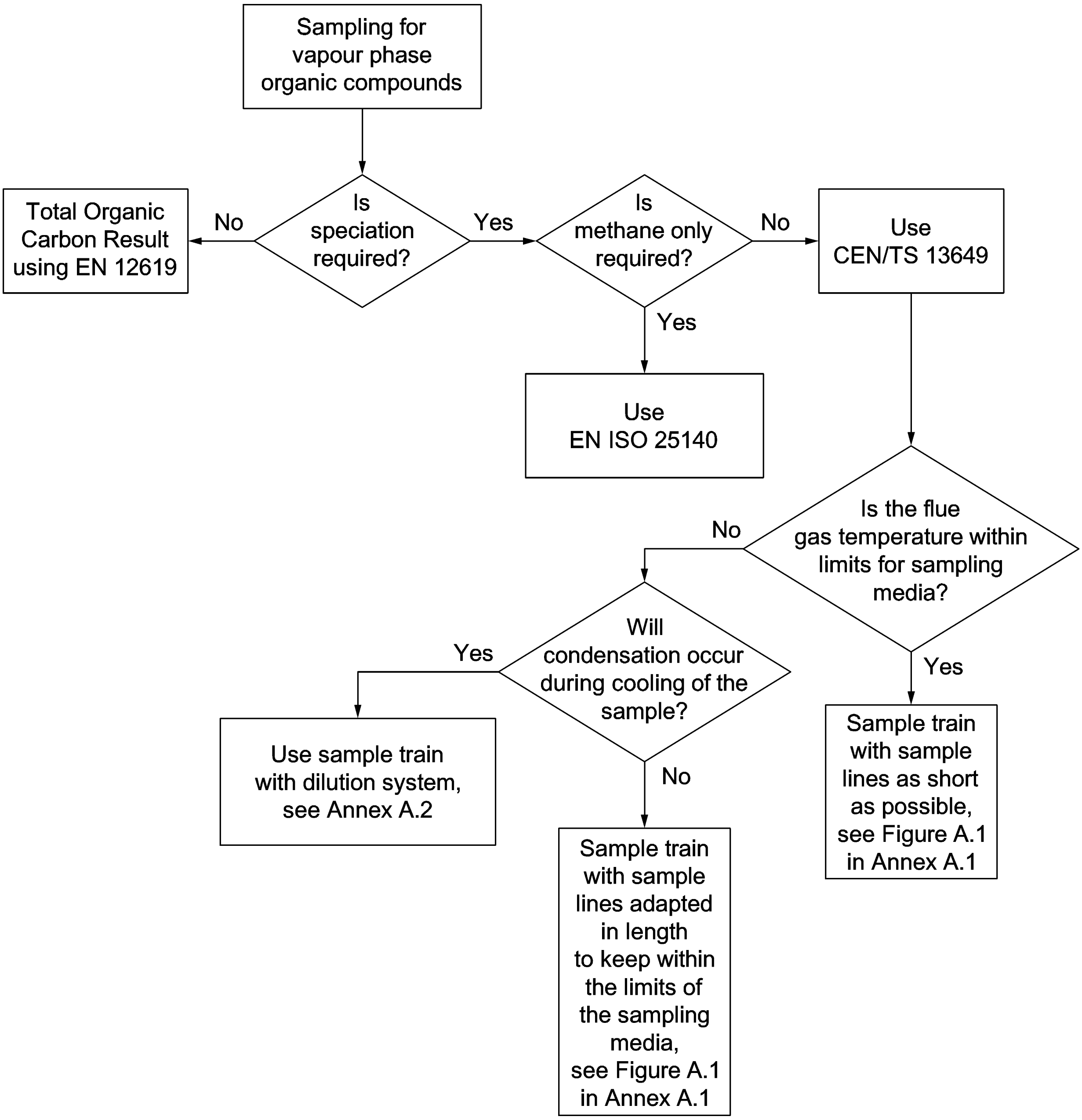


Figure 1 — Decision tree for determination of sampling procedure

Liquid water interferes with the sorption process and shall not be allowed to reach the sorbent material (activated carbon or thermal desorption compatible sorbents). There shall be no visible condensation within the tube.

Drying tubes, e.g. sodium sulfate, shall not be used upstream of the sorbent because of the risk of VOC losses.

Sorbent sampling methods (activated carbon or thermal desorption-compatible) are only compatible with the vapour-phase fraction of semi-volatile compounds. Any particulates in the sample gas shall be entrained on filters before the sample is allowed to reach the sorbent bed.

5.2 Sampling system

The set-up of a suitable sampling system is shown in Annex A.

The sampling system shall be made of materials which are chemically and physically inert to the constituents of the gaseous effluent. Glass, PTFE and polypropylene fluoride or any other material for which it has been shown that they do not absorb or react with compounds present in the sample gas at the temperature considered, are suitable. To avoid contamination from particulate, a dust filter shall be used. This should be heated if necessary, depending on application.

5.3 Sampling tubes

5.3.1 Sampling tubes for solvent extraction

The sorbent tube, filled with activated carbon as the adsorbent, shall have the following characteristics:

- a main adsorbent layer containing 100 mg of activated carbon with a glass wool plug at the front of the tube;
- a security adsorbent layer to detect breakthrough, containing 50 mg of activated carbon separated from the front layer.

Sorbent tubes shall be used in accordance with the manufacturer’s instructions to avoid leakage and sample loss. Open or used carbon tubes shall not be reused.

NOTE A suitable type of tubes is NIOSH type B with closed melted ends.

5.3.2 Sampling tubes for thermal desorption

Stainless steel, inert-coated steel or glass samplers supplied capped and packed with one or more conditioned, thermal desorption compatible sorbents shall be used for organic vapour sampling and subsequent thermal desorption analysis. See Annex C and EN ISO 16017-1 for more details. The sampling end of an identical, secondary (back-up) tube can be connected to the outlet of the primary sampling tube as a check on breakthrough. See 6.3 and Annex C for more information. Unions for connecting the two tubes in series shall comprise inert materials such as stainless steel, coated stainless steel or PTFE and shall not damage tube ends.

NOTE Stainless steel (or inert-coated steel) compression couplings fitted with combined PTFE ferrules have been found to be effective for connecting sample tubes together in series.

Thermal desorption sampling tubes can be re-used many times (typically > 100 thermal cycles).

Conditioned tubes shall be considered sufficiently clean if individual artefact masses do not exceed 10 % of the mass retained when sampling flue gases at the lowest concentration of interest. See also 6.6.

5.4 Pumps and other devices for sampling

A sampling pump or some alternative means of pulling a controlled flow or volume of waste gas through the sampling system and onto the sampling tube is required. The pump or alternative flow controlled sampling system shall have an adjustable flow rate (e.g. up to 0,1 l/min for thermal desorption tubes or up to 0,5 l/min for charcoal tubes); typical flow rate and sample volume ranges for activated carbon and thermal desorption tubes are given in Annex B and Annex C respectively.

As thermal desorption typically offers three orders of magnitude more sensitivity than solvent extraction, it also allows the option of collecting small sample volumes. For example, if individual organic compounds are present above 500 µg/m^3, a sample volume of 100 ml is usually sufficient for thermal desorption/GC analytical sensitivity. Such small aliquots can be accurately drawn onto the sorbent tubes using simple bellows-type pumps or even by slowly withdrawing the plunger of a large gas syringe.

NOTE Such 'grab' sampling methods are only suitable for steady-state emissions. They are not suitable for time weighted average monitoring of variable waste gas concentrations e.g. when monitoring emissions throughout the duration of a specific batch process, unless multiple sequential emission samples are collected.

The pump or alternative sampling mechanism shall be placed downstream of the sorbent tube and coupled to the non-sampling end of the sorbent tube or sorbent tube assembly. See Annex B and Annex C for more information.

5.5 Gas volume meter

The volume of the gas sampled shall be measured using a calibrated device, e.g. gas volume meter or calibrated pump, providing the volume is measured with a relative uncertainty not exceeding 5 % at actual conditions. The uncertainty of the measurement of the temperature and the pressure, shall be less than 2,5 °C and less than 1,0 % respectively.

5.6 Analytical reagents

5.6.1 General

Only reagents of analytical grade or better quality shall be used unless otherwise stated.

5.6.2 Extraction solvent (for solvent extraction)

Extraction solvents, for solvent extraction, shall be of chromatographic quality and free from compounds co-eluting with the compounds of interest.

NOTE Carbon disulphide (CS_2) is a suitable extraction solvent for most of the compounds likely to be encountered in solvent using processes.

Beware of low and variable recovery rates for polar compounds. Use of additional or alternative extraction solvents may improve recovery in these cases.

5.6.3 Reference materials for calibration of the analytical procedure

The chromatographic system shall be calibrated with those reference materials which correspond to the compounds likely to arise in the process under investigation.

For calibrating solvent extraction methods the reference materials shall be prepared in a solution of the extraction solvent to be used. The extraction solvents are highly volatile and fresh reference standards shall be prepared regularly.

For calibrating thermal desorption methods, liquid or gas phase standards may be used. See 7.1.2 and EN ISO 16017-1 for more information.

Liquid standards for thermal desorption should be prepared in a 'carrier' solvent that is free from interfering artefacts. Choose a solvent that can either be selectively purged from tube during the standard loading process (see 7.1.2) or that can be chromatographically resolved from the compounds of interest during analysis.

5.7 Analytical apparatus

5.7.1 Capillary gas chromatograph (GC)

Laboratory apparatus suitable for capillary column gas chromatography shall be used.

5.7.2 Thermal desorber (for thermal desorption)

The thermal desorber is connected to the GC (or GC-MS). It is used for the two stage thermal desorption of sorbent tubes and transfer of the desorbed vapours via an inert gas flow into a gas chromatograph. A typical apparatus contains a mechanism for holding the tubes to be desorbed while they are heated and purged simultaneously with inert carrier gas. The desorption temperature and time is adjustable, as is the carrier gas flow rate. The apparatus should also incorporate additional features such as leak testing, a cold trap in the transfer line to concentrate the desorbed sample and at least one, preferably two quantitative sample split points. The desorbed sample contained in the purge gas, is routed to the gas chromatograph and capillary column via a heated transfer line.

Optional features to be considered include internal standard addition, automatic dry purging for simplifying the analysis of humid samples and re-collection of split flow for repeat analysis and validation of compound recovery (see Annex C).

6 Sampling procedure

6.1 General

The requirements of EN 15259 shall be met.

NOTE The homogeneity tests specified in EN 15259 can be performed using direct read-out FID instruments in accordance with EN 12619 [3] providing the FID signal obtained is representative of the compound of interest.

6.2 Sampling conditions

The test laboratory shall have a documented procedure, to describe how to determine an appropriate sampling volume and time. The temperature of the sample gas reaching the sorbent tube shall not be allowed to exceed 40 °C. The sampling time and volume shall be calculated using

- the estimated concentration and/or limit value,
- the lower limit of detection of the analysis method,
- the safe sampling volume or capacity of the tube for the compounds of interest at the relevant sampling temperature, i.e. a volume of not more than 70 % of the 5 %-breakthrough volume or 50 % of the retention volume,
- the process time e.g. batch process time.

NOTE 1 Sample time and duration may be specified by the regulatory authority.

NOTE 2 If information on total VOC concentration in the waste gas is available from FID or some other stack monitoring device, this can be useful in determining suitable sampling volumes.

Typical sample flow rates and sample volumes for charcoal tubes and thermal desorption are described in Annex B and Annex C respectively.

In all cases, the volume, duration and frequency of sampling shall be sufficient to ensure that the quantitative data obtained is representative of the mean compound concentration in the waste gas for the duration of the process being monitored or over the period of sampling. To ensure representative sampling when collecting small volumes of waste gas, the volume of the sampling system shall be taken into account and flushed with waste gas immediately before the start of sampling.

A continuously flushed sampling system with a ‘Tee-ed’ bypass line can also be used. If compound breakthrough or sample overload are particular concerns due to high compound volatility or high flue gas concentrations; sampled volumes should be minimised. In the case of monitoring steady-state emissions with thermal desorption tubes this can be achieved using simple grab-sampling apparatus (see 5.4). However, for time weighted average monitoring and whenever using pumps or similar flow-controlled apparatus, sampling small waste gas volumes may be subject to higher error – depending on the respective flow rate range of the pump/device selected. In this case, gas dilution should be used to maintain sampling flow rates and volumes at a constant level while minimising risk of sample overload and breakthrough. Dilution can be either static or dynamic (see Annex A).

Sample overload or breakthrough shall be controlled by separate analysis of the second section (activated carbon tubes) or secondary back-up tubes (thermal desorption). See 5.3.2 and Annex B and Annex C for more information. Maximum breakthrough allowed is 5 % of the overall concentration (see Clause 9).

If analytical data obtained from the second layer or secondary (back-up) tube is below the detection limit, it is accepted that there is no breakthrough.

6.3 Measurement of waste gas sample volume

The volume of the gas sampled shall be determined using a calibrated sampling device, see 5.5. See Annex A for details of sample train components.

The sample temperature and pressure at the gas meter shall be measured unless automatically compensated for by the sampling device.

The sample time shall be noted (refer to Clause 10).

6.4 Control of leakage

Leakage contributes significantly to sampling errors and shall be controlled by appropriate check procedures before each sampling run. A suitable procedure for control of leakage is given in Annex A. The leak check shall be carried out before and after sampling.

6.5 Handling, storage, transport of sampled tubes

6.5.1 General

Containers and materials emitting (outgassing) VOC, e.g. wood, certain plastics and sealing tape, shall not be used for sample storage and transport. Tube storage containers shall be clean.

If sampled tubes cannot be analysed within 7 days they shall be stored in an air-tight container at < 4 °C (refrigerated).

All tubes stored under refrigerated conditions, shall be allowed to equilibrate with room temperature before they are removed from their storage container and uncapped for analysis. Allowing the tubes to equilibrate with room temperature prevents ambient humidity condensing inside cold tubes.

6.5.2 Activated carbon (charcoal) tubes

Sampled tubes shall be capped then stored and transported in an airtight VOC free container without exposure to direct sunlight and below 25 °C.

6.5.3 Thermal desorption tubes

Thermal desorption tubes shall be sealed using long term storage caps before and immediately after sampling as specified in EN ISO 16017-1. Once capped, sorbent thermal desorption tubes shall be stored and transported in a VOC free air-tight container without exposure to direct sunlight and below 25 °C.

If sampled thermal desorption tubes are stored under refrigerated conditions, caps shall be retightened after the tubes have reached their minimum storage temperature.

6.6 Blanks

6.6.1 Field blanks

Field blank tubes comprise conditioned sorbent tubes, taken from the same batch as those used for field monitoring, opened and handled in the same manner at the sample location as the sampling tubes but without putting them in the stack or pulling the waste gas through them. They are subsequently analysed with the sampled tubes to determine the average blank level for each compound of interest.

Every measurement campaign shall include at least one field blank per day. When taking more than 6 samples in one day then 2 field blanks are required. For greater than 10 samples in one day then 3 field blanks are required.

In the case of activated carbon tubes it is only necessary to analyse the main adsorption layer of any field or analytical blank.

6.6.2 Analytical (laboratory) blanks

Analytical (laboratory) blanks comprise conditioned samplers (sorbent tubes), taken from the same batch as those used for field monitoring. They shall remain in the laboratory and shall be analysed as a check on inherent sampler cleanliness (see 5.3) and the level of background contamination of the analytical system.

6.6.3 Solvent blank

The cleanliness of any solvent shall be determined prior to use, refer to 5.6.2.

7 Analytical procedure

7.1 Calibration of the GC analysis

7.1.1 GC calibration for analysis of solvent extracts

Calibration solutions shall be prepared using the same extraction solvent that is used for the sample tubes. The range of concentration of the calibration solutions shall cover the concentrations of the sample extracts to be analysed (see 5.6.3). At least five different concentration levels shall be used for calibration.

Calibration solutions with low concentrations of organic compounds can be prepared by first making a stock solution and then by diluting the stock solution to various concentrations. However, extraction solvents are highly volatile and evaporative losses should be minimised by using vessels closed with septa. The amount of the evaporative losses can be determined by weighing the vessels before adding the first organic compound to the extraction solvent and after adding the last organic compound to the extraction solvent. The least volatile organic compound should be added to the extraction solvent first and the most volatile organic compound should be added last. The evaporative losses are the difference between theoretical final weight and real final weight and should be less than 1 % of the theoretical final weight.

Typically 1 µl of each calibration solution should be injected into the GC, operating under the same conditions as for the sample analysis. A calibration graph should be prepared for every organic compound by plotting the area of the compound peaks, on the vertical scale against the mass of the compound, in micrograms, corresponding to the concentration in the calibration solutions.

The calibration Formula (1) shall be determined using linear regression:

$$A_i = f_i \cdot m_i + b_i \tag{1}$$

where

A_i is the measured area of organic component *i*;

f_i is the slope of the calibration line for organic component *i*;

m_i is the mass of organic component *i* in the injected aliquot of sample extract;

b_i is the intercept on the ordinate of the calibration line of organic component *i*.

7.1.2 Calibration for thermal desorption analysis

Thermal desorption methods are normally calibrated by introducing liquid or gas phase standards to the sampling end of blank sorbent tubes in the vapour phase in a stream of carrier gas as described in EN ISO 16017-1.

Liquid standards can alternatively be introduced directly to the sorbent sampling surface within the tube provided care is taken not to dislodge the gauze or other sorbent support mechanism. This approach is particularly suitable for reactive or high boiling compounds. A short purge of pure carrier gas (e.g. 5 min at 30 ml/min) should be applied to the sorbent tube, in the sampling direction, immediately after direct introduction of liquid standards in order to sweep target compound into the sorbent bed and selectively eliminate a significant proportion of the carrier solvent, if applicable (see 5.6.3). The range of compound masses introduced to blank sorbent tubes to make standards shall cover the range of compound masses expected to be retained during sampling (see 5.6.3). At least five different concentration levels shall be used for calibration.

Prepared standard tubes shall be capped and sealed unless they are to be analysed immediately.

The thermal desorption/GC-MS analytical system shall be calibrated over the required concentration range by desorbing sorbent tubes loaded with known masses of target compounds prepared as described above. Plot the calibration curve (peak area vs. mass of compound) for each compound of interest as described in 7.1.1.

7.2 Sample preparation (desorption/extraction)

7.2.1 Solvent desorption

A suitable procedure for desorbing the collected sample is as follows:

- open the sorbent tubes, using a glass cutter if appropriate;
- place the main adsorbent layer with the glass wool plug into a glass vial and the security adsorbent layer into separate glass vial; the foam plug between the two layers may be discarded;
- close the vials with a septum using a screw cap or a crimp cap;
- inject a known volume of CS_2, or another suitable extraction solvent through the septum using a syringe. An amount of 1,0 ml of CS_2 per 100 mg of carbon is sufficient in most cases. The desorption efficiency can be determined as shown in Annex C;
- agitate the vials in an ultrasonic bath for 10 min at a temperature not exceeding 25 °C;

— separate the carbon particles by centrifugation for 10 min; the carbon particles are now at the bottom of the vial. The extract is above and can be taken out by a syringe via the septum of the vessel manually or automatically by a GC sampling system.

NOTE Any unused sample extract can be stored, for example in flame sealed glass Pasteur pipettes in a freezer.

Appropriate safety precautions shall be followed throughout, see Annex E.

7.2.2 Thermal desorption

Uncap the sample tubes and place them in the thermal desorption/GC system sequentially (manual systems) or as a batch with appropriate analytical caps (automated systems). Tubes shall be orientated such that the flow of inert carrier gas used for thermal desorption passes through the tube in the opposite direction to the flow of waste gas during sampling. Sampled tubes shall be interspersed with blanks, mid-level calibrant (standard) tubes and any back-up tubes (used to check for breakthrough during sampling (see 5.3.2)).

Tubes which have been used to sample waste gases with a high moisture content may require purging, in the sampling direction, before analysis in order to remove residual moisture, e.g. with a flow of 50 ml/min to 100 ml/min of pure (>99,999 %) dry air or carrier gas for 15 min, Some commercial thermal desorption auto-samplers allow this dry purging to be carried out automatically as part of the two-stage thermal desorption process. Alternatively, batches of sampled tubes can be dry purged off-line using a suitable apparatus.

Care shall be taken that the sum of sampled and dry purge volumes passing through the sample tube does not exceed the breakthrough volume of any target compound.

7.3 Analysis

7.3.1 GC analysis of extract from activated carbon tubes

The analysis of the sample shall be carried out by capillary gas chromatography (GC) with a flame ionization detector or a mass selective detector. Typically 1 µl of the sample extract should be injected into the GC. The masses m_i of the compounds shall be calculated from peak areas of the chromatogram. The sample extract from the main adsorbent layer and the back adsorbent layer are analysed separately.

7.3.2 Thermal desorption / GC analysis of sorbent tubes

The process of thermally desorbing a tube is fully automated on commercial thermal desorption systems, and involves multiple stages. Once the sorbent tube has been placed in a compatible thermal desorption apparatus it is normally pressurized and sealed to check for leaks without compromising sample integrity. The air inside the tube shall then be purged to vent using carrier gas in order to avoid chromatographic artefacts arising from the thermal oxidation of the sorbent or GC stationary phase. It is usually necessary to use 10 × the tube volume (i.e. 20 ml to 30 ml) of inert gas to completely displace the air in a tube prior to desorption. A larger volume of purge gas may be required to purge the strongest sorbents such as carbon molecular sieves. The tube shall then be heated with carrier gas flowing in the opposite direction to the gas flow during sampling.

NOTE 1 Typically 30 ml/min to 50 ml/min carrier gas flow optimises desorption efficiency.

The desorbed sample occupies a volume of several millilitres of gas so that pre-concentration is essential prior to capillary GC analysis. This can be achieved using a small, moderately- (typically electrically-) cooled, secondary sorbent trap, which can be desorbed sufficiently rapidly at low flow rates (<5 ml/min) to minimize band broadening and produce capillary-compatible peaks.

NOTE 2 When thermal desorption of a solid sorbent sampling tube (primary trap) is used in conjunction with refocusing and thermal desorption of a secondary focusing trap, this is called 2-stage thermal desorption.

NOTE 3 Alternative cryofocusing methods of pre-concentration are available but these typically require cooling to –100 °C or below with liquid cryogen. Cryofocusing also requires tubes to be stringently dry-purged before analysis to prevent ice forming in the cryo-trap and blocking the flow of gas.

Desorption conditions (temperatures, times and carrier gas flows) should be chosen such that desorption from the sample tube, pre-concentration trap and thermal desorption system as a whole is complete (>95 %) (see Annex C). More details of thermal desorption parameter selection are given in EN ISO 16017-1.

To minimize broadening of the chromatographic peaks during analysis, the part of the sample flow path between the focusing trap and the capillary column (or the fused silica retention gap connected to the analytical column), should be short, low-volume and uniformly heated. Various configurations of low volume valving with narrow-bore tubing and/or using minimum dead volume unions have been found to be effective. A split valve is conveniently placed at the inlet and/or outlet of the secondary trap (see 5.7.2). Selected split ratios will vary from several thousand: 1 to zero depending on the mass of target analytes retained on the tube during sampling.

NOTE 4 Most capillary GC columns and detectors work optimally with individual analyte masses of 200 ng or less. Splitting options allow sorbent tubes containing much higher masses of compounds (e.g. several milligrams) to be analysed without overloading the analytical column and detector.

NOTE 5 Some commercial TD systems offer the ability to re-collect all of the split flow thus facilitating repeat analysis and validation of recovery through the TD system (see Annex C).

7.4 Quantification of individual organic compound concentrations

Sampled tubes, back up tubes (where applicable), calibration standards and blanks shall be analysed as described in Annex B or Annex C. In the case of tubes for solvent extraction, both the primary and security layers shall be analysed. The GC peak areas shall be used to determine the mass m_i of each individual compound in the injected / desorbed sample using the respective calibration graphs. Results from the main adsorbent layer and the security adsorbent layer (charcoal tubes) or from the primary and back-up tubes of thermal desorption tube pairs are compared to check if the sample is valid (see 6.2 and Clause 9).

For solvent extraction methods, the mass of the specific compound *i* collected by the sorbent tube can be calculated by multiplying m_i determined by the GC analysis of the extract from main adsorbent layer by the volume ratio of extraction solvent used for the main adsorption layer (determined by weighing, see 7.2.1) to the volume used for the GC analysis. The mass collected on the security layer is calculated in the same way and added.

$$m_{\mathrm{i,t}} = m_{\mathrm{i,ml}} \cdot \frac{V_{\mathrm{em}}}{V_{\mathrm{im}}} + m_{\mathrm{i,sl}} \cdot \frac{V_{\mathrm{es}}}{V_{\mathrm{is}}} - m_{\mathrm{i,ab}} \cdot \frac{V_{\mathrm{eab}}}{V_{\mathrm{iab}}} \tag{2}$$

where

$m_{\mathrm{i,t}}$ is the total sampled mass of component *i*;

$m_{\mathrm{i,ml}}$ is the sampled mass of component *i* on the main layer;

V_{em} is the volume of extraction solvent used for the main layer;

V_{im} is the volume of extraction solvent for the main layer used for GC analysis;

$m_{\mathrm{i,sl}}$ is the sampled mass of component *i* on the security layer;

V_{es} is the volume of extraction solvent used for the security layer;

V_{is} is the volume of extraction solvent for the security layer used for GC analysis;

$m_{\mathrm{i,ab}}$ is the analytical blank of component *i*;

V_{eab} is the volume of extraction solvent used for analytical blank determination;

V_{iab} is the volume of extraction solvent of analytical blank determination used for GC analysis.

In the case of thermal desorption tubes, the mass of compound sampled can be determined directly from the calibration. The mass of compound on the analytical blank tube can be determined in the same way and is usually negligible (<1 % of sampled masses). If the analytical blank level is significant (10 % or more), the mass of compound collected from the sample gas shall be corrected by subtracting the analytical blank.

The value of the field blanks shall be included in the report.

8 Calculation of results

8.1 Concentration

The concentration of the specific compounds in the sampled waste gas, in milligrams per cubic metre, is determined from the measured mass of compound collected divided by the volume of waste gas sampled, referred to standard conditions of temperature, pressure and oxygen if necessary.

8.2 Uncertainty

The overall uncertainty of the measured values shall be calculated in accordance with EN ISO 14956 on the basis of the performance characteristics according to 9.2 performance requirements and shall meet the uncertainty required for the measurement objective.

9 Quality control

9.1 General

When sampling well characterized waste gases, at least a tenth of samples shall be collected using tube pairs (i.e. sampling plus backup tube) or tubes with an integral back-up section as a check on breakthrough. One such tube or tube pair shall be used in each measurement campaign. If > 5 % breakthrough is found to have occurred, the results for these compounds do not meet the requirements of this Technical Specification and shall be treated as semiquantitative (see 6.2).

When sampling uncharacterised waste gases additional tube pairs with back tubes (or tubes with an integral back section) shall be included as check on breakthrough.

The field blank value shall not be deducted from the measured value. The field blank value shall be less than 10 % of the measured value or of the limit value to which the measurement result is to be compared. If the calculated measured value is less than the determined blank value, the result is reported as less or equal to the blank value. When multiple blank values have been determined the highest blank value shall be used.

9.2 Performance requirements

9.2.1 Sampling

Table 1 — Performance requirements for sampling

Description	Requirements/Range	Uncertainty	Clause
Sample flow rate			
Active carbon tubes	0,1 l/min to 0,5 l/min	< 5 %	Annex B
TD	10 ml/min to 100 ml/min	< 5 %	Annex C
Sample volume			
Active carbon tubes	Typically 10 l to 50 l	< 5 %	
TD	Typically 1 l to 5 l	< 5 %	
Field blank value		< 10 % of emission limit value	9.1
Leak rate	Less than 5 % of the sampling flow rate		A.1.2
Breakthrough on 2nd layer or back up tube		< 5 % of the total amount both tube or primary and secondary layer	9.1
Sample gas temperature	< 40 °C	< 2,5 °C	6.2
Sample pressure	Application dependant	1 %	5.5
Heated sample probes (when used)	10 °C above the stack temperature up to a maximum of 180 °C	< 2,5 °C	

9.2.2 Analytical

Table 2 — Performance requirements for analysis

Description	Requirements/Range	Uncertainty	Clause
Cleanliness extraction solvent	Individual artefact masses shall not exceed 10 % of the mass retained when sampling flue gases at the lowest concentration of interest		5.6.2
Cleanliness of TD sampling tubes before sampling	Individual artefact masses shall not exceed 10 % of the mass retained when sampling flue gases at the lowest concentration of interest		5.3.2
Recovery			
Solvent extraction	> 80 %		Annex B
TD	> 95 %		7.3.2 and C.1
Volume of extraction solvent	1,0 ml	< 1 %	7.2.1, bullet 4

10 Report

The test report shall refer to this Technical Specification, and shall include the following information in addition to the report requirements of EN 15259:

a) identification of the sample;

b) analysis results for the security tubes/layers and any instance of > 5 % breakthrough shall be reported and stated that it is an invalid test;

c) measurement values with a corresponding field blank of which is above 10 % of the limit values shall be reported as invalid.

The report should also contain the results of any checks (including sampling system leak checks (see A.1.3)), the desorption efficiency of the main compounds analysed and the proportion of sample recovered from the sorbent tube security layer or backup tube.

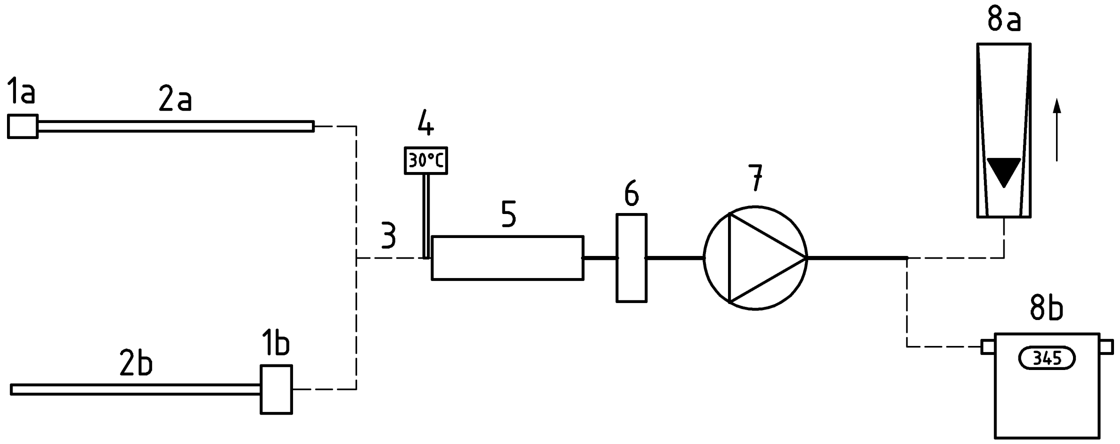
Annex A
(normative)

Sample trains

A.1 Sample train and procedure using thermal desorption or activated carbon tubes

A.1.1 General

Figure A.1 shows the example of a suitable sample train.



Key

1a	in stack particulate filter
or	
1b	out stack heated filter
2a	sample probe, heated depending on application
2b	heated sample probe
3	sampling line, short as possible
4	temperature indicator
5	solid media sorbent media
6	drying unit to protect pump and flowmeter (recommended for wet gases)
7	pump
8a	rotameter (variable area flowmeter)
or	
8b	dry gas meter (or suitable measuring device)

Figure A.1 — Example sample train

A.1.2 Sampling procedure

Refer to Clause 6 of this document.

A.1.3 Leak check procedure

Leaks occur most frequently in the couplings between different components in the sampling line, e.g. defective packings, loose screw connections and broken ground glass joints. Leaks shall be controlled to a level below the uncertainty of the sample volume measurement or less than 5 % of the sampling rate, when tested under the highest vacuum to be applied during sampling. The leak test shall cover the assembly of all compounds of the sampling equipment, from the probe to the gas meter. Different procedures for leak testing can be required, depending on the sampling system used, an example is: The nozzle of the probe is stoppered and the pump started. After the maximum working vacuum is obtained the leak rate is measured with a flow meter, or the volume increase on the gas meter.

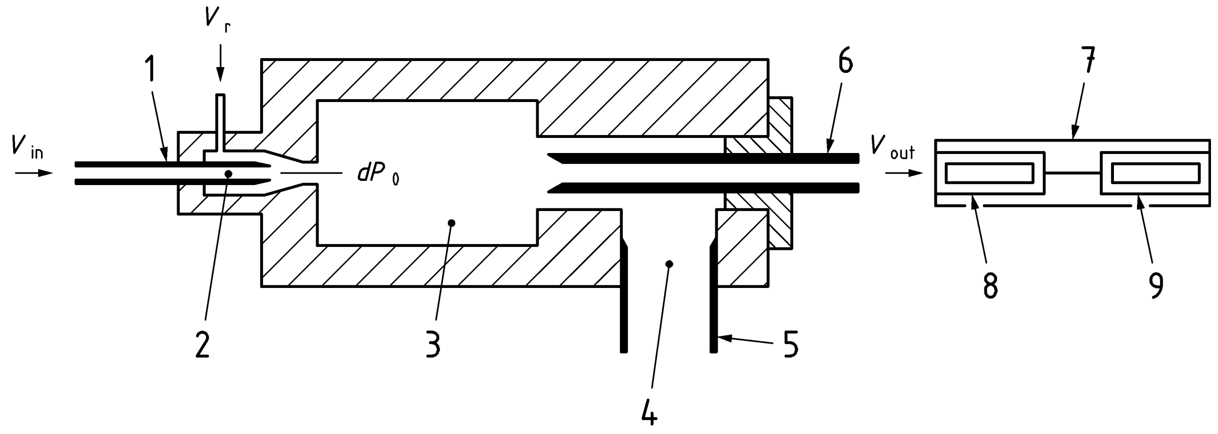
A.2 Sample train and procedure using dilution sampling with sorbent sampling tubes

A.2.1 Procedure for dynamic dilution

Many of the solvent using processes covered by the Industrial Emissions Directive produce waste gases which do not have a high water content. This document requires the use of a dilution sampling system when the concentration of water or solvent is high enough to cause the risk of condensation. A suitable system is shown in Figure A.2. Clean dry air or nitrogen are suitable dilution gases.

Procedure:

- — Connect a supply of dilution gas to the sampling system.
- — Set the flow of dilution gas to a known volumetric flow.
- — Sample a measured volume of waste gas at a known volumetric flow.



Key

1	inlet nozzle
2	annular nozzle
3	mixing chamber
4	excess mixture outlet
5	excess mixture tube connector
6	outlet nozzle
7	sorbent tube
8	main layer
9	security layer

Figure A.2 — Example of a dynamic dilution system

Hydrocarbon free air, e.g. synthetic air from a gas cylinder with the controlled and constant volume flow V_r circulates through an annular passage around the suction nozzle. Thus, according to Bernoulli, a defined volume flow V_{in} is generated in the suction nozzle and sucks in the waste gas to be analysed. At the outlet nozzle a constant volume flow V_{out} is taken for the provided analysis. The mixture which cannot be used with V_{out} goes out via the excess mixture outlet.

The dilution factor F_d is calculated by:

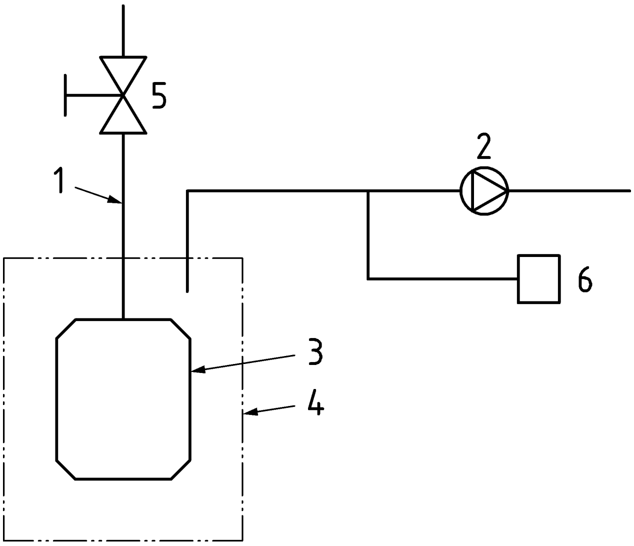
$$F_d = \frac{V_r + V_{in}}{V_{in}} \tag{A.1}$$

A.2.2 Procedure for static dilution

Static dilution sampling can be carried out by part filling a sample bag, fabricated from an inert material, with a known volume of dry dilution gas, a known volume of flue gas is then added. A heated sampling probe can be used to ensure that no condensation occurs before the sample enters the bag. The bag is then emptied through the sorbent tube.

A suitable procedure is the ‘lung principle’ in which a sample bag is placed in a rigid, leak proof container, the air is removed from the container using a vacuum pump, the reduced pressure in the container causes the bag to fill with a volume of sample equal to that which has been removed from the container. A pressure control device operating at not greater than 250 Pa should be used to prevent the bag bursting.

A suitable bag material is polyvinyl fluoride.



Key

1	PTFE tube
2	pump
3	bag (partially filled with dilution gas)
4	rigid container
5	PTFE valve
6	pressure control device

Figure A.3 — Example of a static dilution sampling system

A suitable pre-dilution procedure for use with this Technical Specification is as follows:

- Place a flexible sample bag in a rigid container (see Figure A.3).
- Fully inflate bag with dilution gas (dry clean air or nitrogen is suitable).
- Attach a calibrated gas meter to the bag, record gas meter reading.
- Fully deflate bag and record the meter reading.
- Fully inflate bag with dilution gas.
- Remove a known volume of dilution gas.

- Collect a sample at a suitable flow rate, the sample collection is complete when the pressure control device activates.
- Sample humidity should be measured in order to determine the dry gas volume for the calculation of the concentrations (see 8.1).

Annex B
(informative)

Solvent extraction of activated charcoal tubes

Solvent extraction is suitable for measuring individual VOC ranging in concentration from 0,5 mg/m^3. The upper end of the range is limited by breakthrough during sampling and the analytical conditions selected.

The desorption efficiency shall be greater than 80 %. If it is lower than 80 % the use of different extraction solvent is advisable. For non-polar substances carbon disulfide is the best extraction solvent.

For polar substances diethyl ether, carbon disulfide/2-propanol mixture or dichloromethane/methanol mixtures may be more suitable.

The desorption efficiency for the particular batch of carbon used for sample collection shall be determined for the substances of interest over the expected concentration range. Test samples shall be prepared by injecting a known quantity of calibration solution (stock solution), in a stream of pure nitrogen or helium of 0,1 l/min, onto the carbon in the tube. After this, the tube shall be purged for 10 min. Then this spiked tube shall be capped immediately and stored for 7 days to simulate real field monitoring conditions. At least 5 tubes shall be prepared in this manner. A parallel blank tube shall be treated in the same manner except that no stock solution is added to it. The spiked tubes and blank tubes shall be extracted and analysed in exactly the same manner as the sampling tubes. The desorption efficiency of each substance is the ratio of the mass of recovered substance to the mass of substance added to the carbon adsorbent expressed as a percentage.

Open or used sorbent tubes shall not be reused. Sorbent tubes shall be used in accordance with the manufacturer's instructions to avoid leakage and sample loss.

The typical volume flow rate used for activated carbon tubes (100 mg) is 0,1 l/min to 0,5 l/min and typical sample volumes range from 10 l to 50 l.

Annex C
(informative)

Additional information on flue gas sampling using thermal desorption tubes

C.1 Tube and sorbent selection

Thermal desorption is suitable for measuring individual VOC ranging in concentration from 0,005 mg/m^3. The upper end of the range is limited by breakthrough during sampling and the analytical conditions selected.

Typically, but not exclusively, sorbent tubes for thermal desorption analysis are constructed of stainless steel or inert-coated steel, 6,4 mm (1/4-inch O.D, with 5 mm I.D. and 3,5-inch (89 mm) length. Glass tubes of the same external dimensions, typically have an I.D. of 4 mm. Tubes of other dimensions may be used but tubes of the size described are compatible with most commercial thermal desorption systems and can be directly related to the safe sampling volumes (SSVs) listed in key standards such as EN ISO 16017-1 (see 6.1). Unlike charcoal, most thermal desorption sorbents are hydrophobic and will allow selective elimination of vapour-phase water. Sorbent choice will depend on the volatility range of the compounds of interest.

The available range of thermal desorption sorbents allows this method to be used for vapour-phase organic compounds ranging in volatility from vinyl chloride, C_3-hydrocarbons and freons to the vapour fraction of semi-volatiles such as PAHs, PCBs, phthalates and hydrocarbons to n-C_{36} and above. Thermal desorption is also applicable to a wide range of chemical groups including; hydrocarbons, halogenated hydrocarbons, esters, ketones, aldehydes (except formaldehyde), alcohols, volatile organic acids, glycol ethers, nitriles, sulphides, mercaptans and amines. As a general rule, thermal desorption / GC-MS methods can be used for measuring the vapour-phase fraction of any volatile or semi-volatile organic compound that is compatible with conventional gas chromatography. Assuming appropriate sorbents have been selected for sampling thermal desorption methods readily facilitate > 95 % recovery.

Recovery of sampled analytes from the selected sorbent tube shall be evaluated by desorbing a representative number of sampled tubes twice. If 5 % or more of one or more analytes is observed during the second desorption of a sampled tube, the primary desorption is shown to have been incomplete. If this happens, an alternative, weaker sorbent shall be selected for the sampling tube and/or the analytical desorption parameters shall be amended accordingly.

Recovery of analytes through the thermal desorption analytical system shall also be evaluated. This is especially important for semi-volatiles and thermally labile compounds like some sulfur compounds and reactive amines. Recovery can be evaluated by comparing the thermal desorption / GC-MS calibration curve with that obtained from direct liquid injection of the standard into the same GC-MS (see EN ISO 16017-1.) Alternatively, if the thermal desorption apparatus accommodates re-collection of split flow for repeat analysis, a sequence of repeat analyses can be carried out on a single standard. Any bias that develops for one or more compounds during the sequence of repeat analyses is indicative of selective losses in the system. Amend the desorption parameters accordingly.

Thermal desorption tubes cannot contain two, separately-analysed sections and therefore two tubes shall be connected together in series to assess for breakthrough (see below and see also 5.3.2 and 6.3) during quality control (see Clause 9).

Extensive information on sorbent selection for thermal desorption methods is given in EN ISO 16017-1.

Sorbents and combinations of sorbents which are compatible with thermal desorption and which have been found useful for monitoring individual organic compounds in stack gases are listed below together with the typical sorbent bed length used in each case:

- Tenax TA® (>40 mm): Used for toluene and compounds of equal or lower volatility;
- Carbograph 1 TD™ (>40 mm): used for compounds ranging in volatility from n-$C_{5/6}$ to n-C_{14};
- Carbograph 5 TD™ or Carbopack X™ (>40 mm): used for compounds ranging in volatility from 1,3-butadiene to toluene;
- Quartz wool (approximately 5 mm) backed up by Tenax TA (approximately 35 mm) backed up by Carbograph 5 TD™ (approximately 20 mm): used for vapour phase compounds ranging in volatility from 1,3-butadiene to n-C_{32};
- Carbograph 1 TD™ (approximately 40 mm) backed up by Carboxen 1003™ or Carbosieve SIII™ (approximately 20 mm): used for compounds ranging in volatility from freons and vinyl chloride to n-C_{14}. Note that this sorbent combination is not completely hydrophobic and will require dry purging before analysis if used to sample humid gases.

If more than one sorbent is required to trap and release the volatility range of compounds of interest, the sorbents shall be arranged in series with the weakest sorbent first (i.e. with the weakest sorbent near the sampling end.) If the sorbents required for a monitoring exercise can all be conditioned at the same temperature, they can all be packed into one tube allowing a complete analysis to be achieved in one run. This is true for all the examples listed above. If preferred, each different sorbent can be packed into separate thermal desorption tubes which are then linked together for sampling using inert, stainless steel compression couplings and PTFE ferrules. After sampling the tubes are separated, capped and analysed individually.

While the sorbent retention volumes quoted in EN ISO 16017-1 are for sampling at 20 °C, gas volumes collected for stack emission testing are typically lower than those used in workplace or ambient air. The negative effect of higher sample gas temperatures is thus usually offset by the smaller sample volumes.

As a general rule, retention volumes halve for every 10 °C rise in temperature.

Thermal desorption-compatible sorbent tubes may be packed by the laboratory or are available pre-packed from multiple commercial sources. They can be reused many times (typically > 100 thermal cycles). The process of thermal desorption cleans the tubes so that they can often be re-used without reconditioning.

Care shall be taken to prevent higher boiling analytes from coming into contact with strong sorbents during sampling as this can lead to incomplete recovery during analysis. At least one in 10 sampled tubes and a minimum of one sampled tube in every monitoring exercise should be desorbed twice as a routine check on analyte recovery from the sample tube (see above).

The sorbent bed lengths listed above are presented for guidance only and apply to the types of tubes described above.

Very volatile or volatile polar compounds will require stronger sorbents and or smaller sampling volumes.

C.2 Sampling

If using a pump for time weighted average monitoring, typical flow rates for thermal desorption tubes are 10 ml/min to 100 ml/min and typical sampling volumes ranging from 1 l to 5 l. Possible pump flow rates range from 10 ml/min to 500 ml/min. 'Grab' samples of smaller volumes (e.g. 100 ml) may be collected using low cost bellows-type pumps or by slowly withdrawing the plunger of a large gas syringe attached to the non-sampling end of the sorbent tube using clean, flexible tubing (see 5.4).

Breakthrough shall be checked using two identical sorbent tubes connected together in series (see 5.3.2) during quality control (see Clause 9). This is especially important when using thermal desorption tubes to sample solvent emissions with incomplete prior information of the composition and concentration of VOCs present. The sampling end of the back-up tube shall be connected to the outlet end of the front tube using an inert stainless steel union with combined PTFE ferrules. The pump or alternative sampling mechanism is then attached to the outlet end of the back-up tube such that waste gas can be pulled/pumped through the whole assembly.

Annex D
(informative)

Validation of monitoring methods for speciated organic substances in stack gas

D.1 General

The vast number of compounds emitted by the large variation of processes defined in the BREF documents precludes complete validation of every compound on all different processes.

Below is information that is currently available.

D.2 Background information

D.2.1 General comments

In an ideal world, European Standards should be validated by multiple laboratories. Tests should cover every compound of interest and all the application scenarios covered under the scope by evaluating relevant, well-characterized field examples. For CEN/TS 13649 this would mean using a range of different industrial stacks representative of multiple different industrial processes each containing independently verified concentrations of every analyte of interest in the flue gas.

The challenge for thorough validation of CEN/TS 13649 is that hundreds of compounds of interest are listed in relevant BREF notes and that the possible range of flue gas monitoring scenarios (i.e. analyte mix, concentrations, temperature, humidity, particulate concentrations, inorganic gas composition, etc.) is almost limitless.

D.2.2 Critique of existing EN 13649 validation data

The first edition of EN 13649:2001 only specified charcoal/CS_2 extraction methods and was the subject of a limited validation exercise. Key concerns have been discussed extensively and include the fact that only one (dry) stack was studied, no independent measurement method was employed to verify analyte concentrations in the flue gas, only 2 laboratories were involved and only a limited number of compounds were subjected to all the tests.

D.2.3 Precedents for the parallel acceptance of solvent extraction SE and TD methods

Given that optimization of the sampling process is essentially the same for both types of sorbent tubes and requires consideration of the same sampling parameters, the 2 approaches only differ in terms of the subsequent extraction. It is therefore helpful to consider other vapour-sampling applications where either SE or TD methods are allowed. Key examples include:

- Workplace air:
  - EN 1076 (TD and SE) [4]
  - EN ISO 16017-1 and EN ISO 16017-2 (TD) [5] and ISO 16200-1 and ISO 16200-2 (SE) [6]
  - ASTM D6196 (TD) [7] and ASTM D3686/D3687 (SE) [8; 9]
  - UK Health and Safety Lab MDHS 72 and 80 (TD) [10; 11]; MDHS 88 and 96 (SE) [12; 13]

  - NIOSH series of standards (predominantly SE but some TD)
- Indoor air
  - EN ISO 16017-1 and −2 (TD) [5] and ISO 16200-1 and −2 (SE) [6]
  - ASTM D6196 (TD) [7] and ASTM D3686/D3687 (SE) [8; 9]
  - ISO 16000-6 (TD) [14]
- Ambient air
  - EN 14662 (Parts 1 and 4 (TD), Parts 2 and 5 (SE)) [15]
  - EN ISO 16017-1 and −2 (TD) [5]
  - ASTM D6196 (TD) [7] and ASTM D3686/D3687 (SE) [8; 9]
  - US EPA Method TO-17 (TD) [16]
- Industrial emissions
  - US EPA Method 18 (TD and SE) [17]
  - US EPA Method 0031 – VOST tubes (TD) [18]
  - UK Environment Agency Method LFTGN 04 for landfill gas (TD) [19]
  - EN 13649:2001 (SE)
  - ISO 16000-6 (TD) [14]

It is clear from these examples that thermal desorption and solvent extraction methods are used as alternative sampling and sample preparation methods for a wide number of vapour monitoring applications including stack gas testing.

D.3 Validation for thermal desorption based methods and correlation with solvent extraction procedures

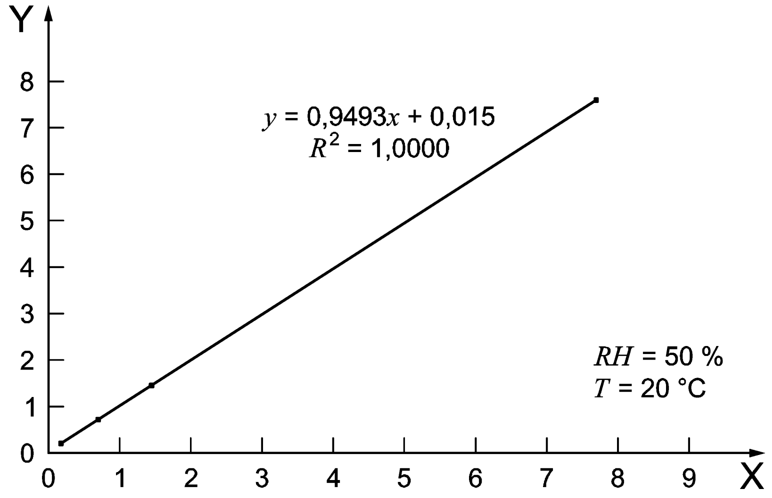
D.3.1 General

During the process of revising EN 13649 a number of studies was collated demonstrating the correlation of thermal desorption and solvent extraction based monitoring methods for speciated organic vapours and the applicability of thermal desorption methods to the type of ‘atmospheres’ presented by flue gas.

D.3.2 First NPL study – validation of TD methods against standard atmospheres

Tests were carried out using the ‘Controlled atmosphere test facility’ (CATFAC) at the UK National Physical Laboratory’s (NPL) central laboratory in Teddington, London. A summary of the experiments carried out is presented in bullet form below:

- Variables tested include: compounds, compound concentrations, CATFAC fan speed and air/gas humidity
- Benzene was validated (R^2 = 1,000) versus independent chamber concentration measurement (see Figure D.1)



Key

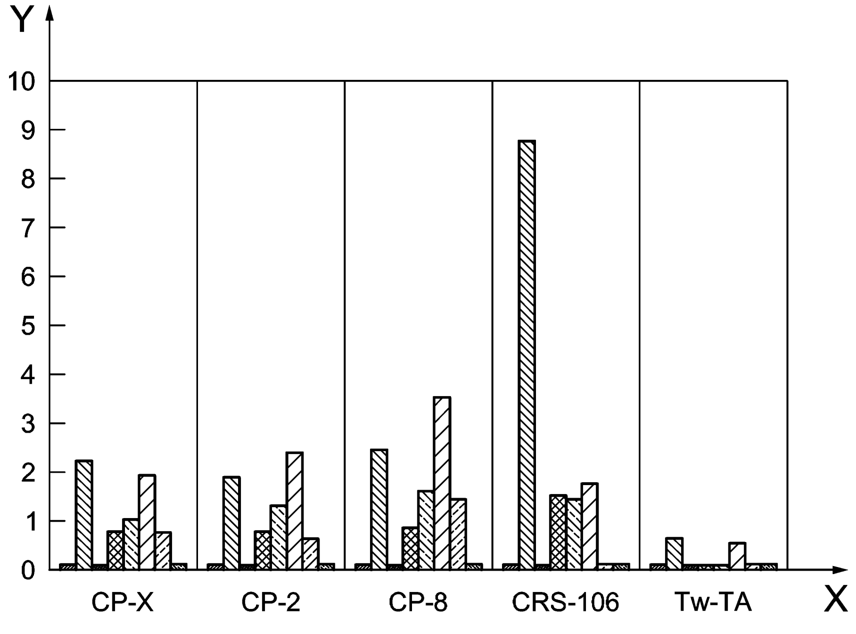
X applied concentration in ppb

Y sampler concentration in ppb

Figure D.1 — Comparison of benzene concentrations from pumped samplers and test atmospheres

— Other parameters examined include:

- — blank levels of common compounds (i-butane, n-butane, i-pentane, n-pentane, n-hexane, benzene, toluene and m-xylene) on various thermal desorption sorbents (Carbopack X, Carbopack Z, Carbopack B and Tenax TA), see Figure D.2.

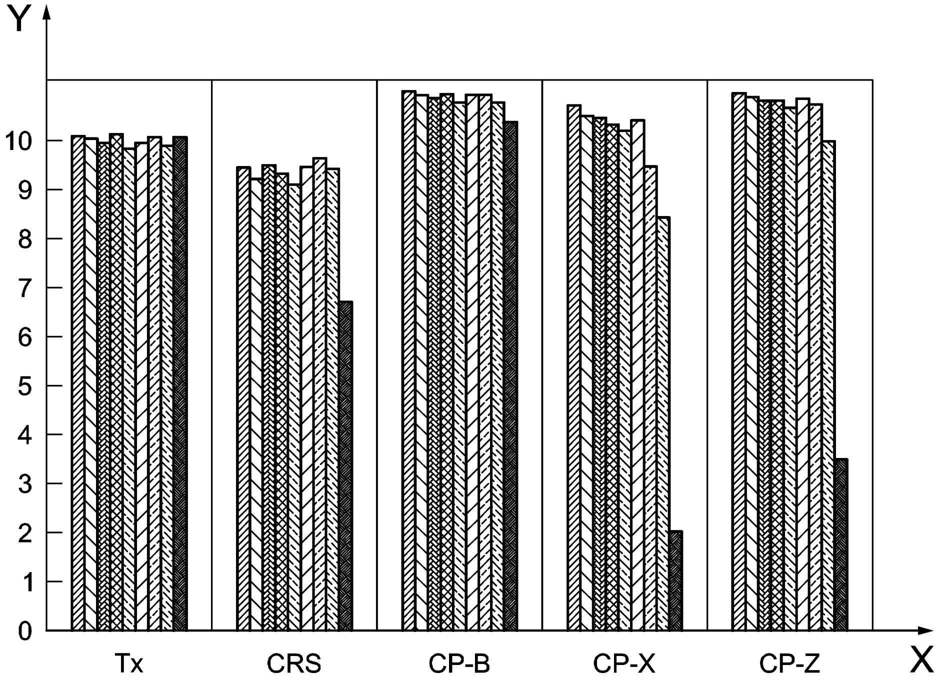


Key

▨	i-butane	▧	n-hexane
▧	n-butane	▨	benzene
■	i-pentane	▨	toluene
▩	n-pentane	▦	m-xylene
X	sampler	**Y**	mean mass in ng

Figure D.2 — Blank levels

- recovery on storage (Sorbents tested: Tenax TA, Chromosorb, Carbopack B, Carbopack X and Carbopack Z; Compounds tested: toluene, m-xylene, n-C9, n-C10, n-C11, n-C12, n-C13, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and naphthalene), see Figure D.3



Key

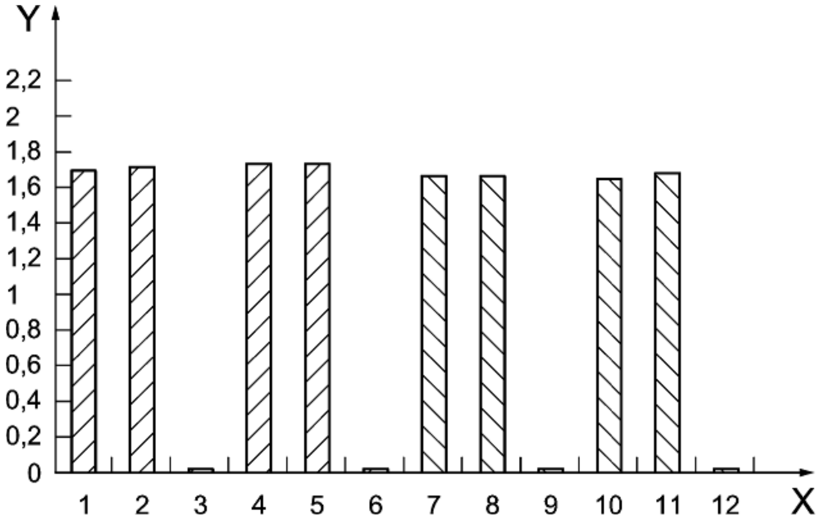
▨	toluene
▧	m-xylene
■	n-nonane
▩	1,3,5-trimethylbenzene
▧	1,2,4-trimethylbenzene
▨	n-decane
▨	n-undecane
▩	naphthalene/dodecane
▩	n-tridecane
X	sampler
Y	recovery in %

Figure D.3 — Storage tests over 14 days

- and impact of humidity (tested using Carbopack X sorbent using n-butane, i-pentane, n-pentane, n-hexane, benzene, toluene and m-xylene), see Table D.1 and Figure D.4

Table D.1 — Concentration of trace species in the CATFAC

Compound	RH = 0 %			RH = 80 %		
	Gas chromatography ppb	**Dilution ppb**	**CP-X Pumped Samplers ppb**	**Gas chromatography ppb**	**Dilution ppb**	**CP-X Pumped Samplers ppb**
n-butane	1,74 ± 0,06	1,83 ± 0,08	1,83 ± 0,17	1,76 ± 0,33	1,79 ± 0,09	1,30 ± 0,14
i-pentane	3,34 ± 0,09	3,33 ± 0,15	3,47 ± 0,28	3,31 ± 0,11	3,27 ± 0,16	3,28 ± 0,23
n-pentane	1,68 ± 0,12	1,67 ± 0,08	1,74 ± 0,14	1,67 ± 0,13	1,64 ± 0,08	1,68 ± 0,11
n-hexane	1,68 ± 0,12	1,67 ± 0,08	1,72 ± 0,14	1,62 ± 0,12	1,64 ± 0,08	1,67 ± 0,11
benzene	1,74 ± 0,05	1,74 ± 0,08	1,74 ± 0,16	1,73 ± 0,07	1,71 ± 0,09	1,69 ± 0,13
toluene	1,71 ± 0,05	1,76 ± 0,08	1,79 ± 0,14	1,64 ± 0,11	1,73 ± 0,09	1,73 ± 0,12
m-xylene	1,53 ± 0,05	1,71 ± 0,08	1,93 ± 0,16	1,47 ± 0,15	1,68 ± 0,09	1,82 ± 0,12



Key

X sampler number

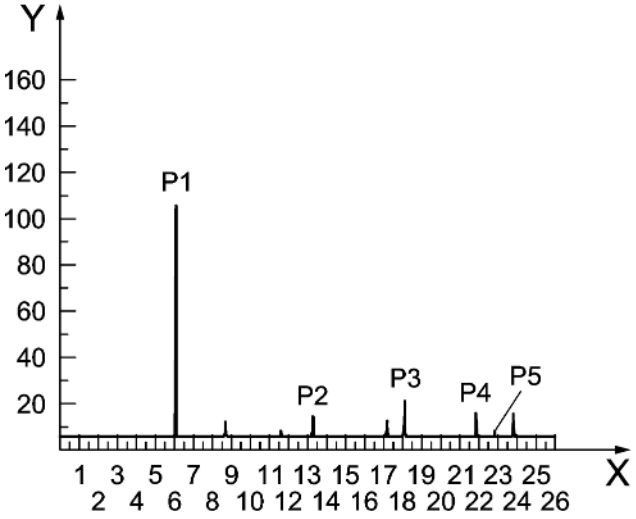
Y concentration in ppb

Samplers 1, 2, 4, 5: RH = 0 %, CATFAC conc. = 1,67 ppb, mean conc. = 1,72 ppb

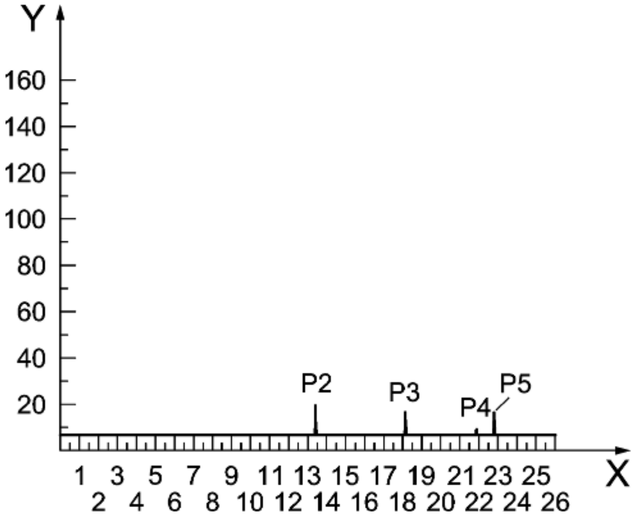
Samplers 7, 8, 10, 11: RH = 80 %, CATFAC conc. = 1,64 ppb, mean conc. = 1,67 ppb

Figure D.4 — Pumped CP-X sampler results for n-hexane

— Other aspects evaluated include the validity of loading liquid vs. gas-phase standards onto thermal desorption sorbent tubes, see Figures D.5 and D.6.



a) Liquid loaded sampler

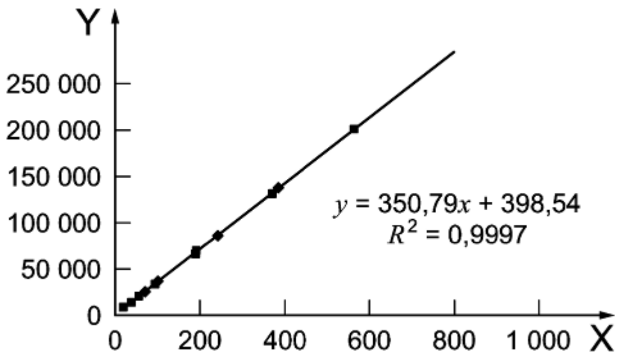


b) Gas loaded sampler

Key

P1	methanol solvent peak	P4	m-/p-xylene
P2	benzene	P5	o-xylene
P3	toluene		
X	time in min		
Y	response in mV		

Figure D.5 — Chromatogram from liquid and gas loaded samplers



Key

X mass in ng

Y area in µV·s

Figure D.6 — Chromatographic areas for benzene gas and liquid loaded samplers versus dosed amounts

More information on these and other similar experiments carried out by National Physical Laboratory can be found in [20] and [21]. These papers demonstrate the efficacy of thermal desorption for the sampling and analysis of VOCs in gas samples.

D.3.3 Second NPL study – validation and comparison of thermal desorption and solvent extraction methods using standard gases

A direct comparison of thermal desorption and solvent extraction methods, was carried out at NPL during August and September 2012.

Thermal desorption tubes containing Carbopack X and solvent desorption tubes containing 100/50 mg of Ansorsb CSC coconut charcoal (SKC) were loaded using NPL certified gas mixtures. For the first test an approximate 1 ppm gas standard was sampled and for the second exercise an approximate 100 ppm standard was diluted to approximately 1/10th of its original concentration. As thermal desorption is a more sensitive technique, these tubes were loaded with approximately 1/10th of that loaded onto the solvent desorption tubes in each case. In the first test exercise approximately 10 µg of benzene and toluene were loaded onto the solvent desorption tubes while approximately 1 µg of benzene and toluene were loaded onto the thermal desorption tubes. In the second test, approximately 100 µg of benzene, 2,2-dimethylbutane, 2-methylpentane and 3-methylpentane were loaded onto the solvent desorption tubes and 10 µg of benzene, 2,2-dimethylbutane, 2-methylpentane and 3-methylpentane were loaded onto the thermal desorption tubes.

The system used for loading the tubes had 12 sampling ports; the tubes were therefore loaded in sets of six tubes of each type alternately positioned in the ports. The test atmosphere was flowed through the system under atmospheric pressure and known volumes of gas were drawn through the tubes using a calibrated personal sampling pump. For both tube types the same make and model of pumps were used.

In Test 1 three batches (6 tubes of each type) were loaded. The first two batches were sampled at the same rate, 20 ml/min for the thermal desorption tubes and 200 ml/min for the charcoal tubes for 15 min, with the third batch being sampled at 20 ml/min for 15 min for the thermal desorption tubes and 100 ml/min for 30 min for the charcoal tubes. In Test 2 two batches (6 tubes of each type) were loaded. These two batches were sampled at the same rate, 20 ml/min for the thermal desorption tubes and 200 ml/min for the charcoal tubes for 15 min in each case.

The analyte masses introduced were calculated using gas concentration and the volume sampled. The measured data are given in µg and for comparison purposes the gas-phase concentration in mg/m^3 has been calculated using the measured data µg values and the sample volume. The actual gas-phase concentration is given at the bottom of each table. Outliers have been highlighted in italics and have been excluded from all calculations. If one species in a data set has an outlier, then all of that data has been excluded. The results are given in Tables D.2 to D.7.

Table D.2 — Thermal desorption results (Test 1)

			Benzene				**Toluene**			
	Sample	**Sample vol. ml**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**
	CX 1336–2	Blk.		< 1				< 1		
	CX 519–2	Blk.		< 1				< 1		
Batch 1	CX 184–2	308,2	1,03	1,01	–1,70	3,29	1,17	1,03	–12,09	3,34
	CX 3753–2	289,1	0,97	0,96	–0,84	3,32	1,10	1,14	3,71	3,93
	CX 578–2	302,7	1,01	1,00	–1,73	3,29	1,15	1,16	0,77	3,82
	CX 3861–2	302,5	1,01	0,99	–2,42	3,27	1,15	1,14	–0,57	3,77
	CX 849–2	303,7	1,02	0,98	–3,15	3,24	1,15	1,12	–2,48	3,70
	CX 92–2	305,9	1,02	1,00	–1,99	3,28	1,16	1,17	0,74	3,82
Batch 2	CX 522–2	309,3	1,04	1,00	–3,14	3,24	1,17	1,19	1,35	3,85
	CX 3853–2	*289,1*	*0,97*	*0,90*	*–6,90*	*3,12*	*1,10*	*0,51*	*–53,47*	*1,77*
	CX 581–2	302,0	1,01	1,02	1,35	3,39	1,15	1,19	3,48	3,93
	CX 357–2	304,6	1,02	0,98	–3,53	3,23	1,16	1,16	–0,02	3,79
	CX 647–2	303,8	1,02	0,98	–3,66	3,22	1,15	1,17	1,34	3,85
	CX 1130–2	*307,5*	*1,03*	*1,01*	*–1,63*	*3,29*	*1,17*	*0,87*	*–25,77*	*2,82*
Batch 3	CX 2587–2	616,0	2,06	2,04	–1,34	3,30	2,34	2,33	–0,54	3,78
	CX 1132–2	576,2	1,93	1,85	–3,92	3,22	2,19	2,14	–2,16	3,71
	CX 3273–2	601,5	2,01	1,95	–3,34	3,24	2,28	2,26	–0,88	3,76
	CX 3580–2	607,5	2,03	1,97	–3,09	3,25	2,31	2,32	0,64	3,82
	CX 3245–2	605,1	2,03	1,96	–3,43	3,23	2,30	2,26	–1,44	3,74
	CX 1196–2	613,7	2,06	2,02	–1,51	3,30	2,33	2,24	–3,83	3,65
min.					–3,92				–12,09	
max.					1,35				3,71	
Range					–5,28				–15,80	
Average						3,27				3,77
Actual						3,3				3,79
Standard deviation						0,05				0,14
2 × Standard deviation						0,09				0,28

Table D.3 — Solvent desorption results (Test 1)

			Benzene				Toluene			
	Sample	**Sample vol. ml**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**
	3862540379	Trv.Blk.		< 1				< 1		
	3862540381	Trv.Blk.		< 1				< 1		
Batch 1	3862540036	3069,0	1,03	9,3	–9,44	3,03	11,6	11	–5,53	3,58
	3862540037	3027,0	0,97	9,3	–8,18	3,07	11,5	11	–4,21	3,63
	3862539626	3058,2	10,2	8,7	–14,98	2,84	11,6	9,8	–15,53	3,20
	3862539628	3007,5	10,1	9,4	–6,59	3,13	11,4	11	–3,59	3,66
	3862539629	3020,9	10,1	9,0	–10,96	2,98	11,5	10	–12,75	3,31
	3862539630	2926,0	9,8	9,5	–2,97	3,25	11,1	11	–0,91	3,76
Batch 2	3862539631	3072,7	10,3	9,5	–7,63	3,09	11,7	11	–5,67	3,58
	3862539633	2976,8	10,0	9,2	–7,67	3,09	11,3	11	–2,63	3,70
	3862539632	3047,5	10,2	9,4	–7,85	3,08	11,6	11	–4,89	3,61
	3862539635	2992,1	10,0	9,0	–10,14	3,01	11,4	11	–3,13	3,68
	3862540038	3024,4	10,1	8,5	–16,04	2,81	11,5	10	–12,88	3,31
	3862540039	*2921,9*	*9,8*	*3,0*	*–69,33*	*1,03*	*11,1*	*3,5*	*–68,44*	*1,20*
Batch 3	3862540040	2938,7	9,84	8,8	–10,58	2,99	11,16	10	–10,38	3,40
	3862540041	2992,8	10,02	9,0	–10,21	3,01	11,36	10	–12,00	3,34
	3862540042	3218,9	10,78	9,9	–8,16	3,08	12,22	12	–1,82	3,73
	3862540043	3019,3	10,11	9,3	–8,03	3,08	11,46	11	–4,05	3,64
	3862540044	3051,1	10,22	9,1	–10,94	2,98	11,59	11	–5,05	3,61
	3862540045	3018,6	10,11	9,3	–8,00	3,08	11,46	11	–4,03	3,64
min.					–16,0				–15,5	
max.					–3,0				–0,9	
Range					13,1				14,6	
Average						3,0				3,6
Actual						3,3				3,3
Standard deviation						0,10				0,17
2 × Standard deviation						0,20				0,34

Table D.4 — Thermal desorption results (Test 2)

			Benzene				**2,2-Dimetylbutane**			
	Sample	**Sample vol. ml**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**
Batch 1	CX 532–2	305,6	9,36	9,01	–3,66	29,50	10,43	10,65	2,11	34,84
	CX 3230–2	292	8,94	8,54	–4,51	29,24	9,96	10,09	1,27	34,55
	CX 83–2	300,9	9,21	8,98	–2,47	29,86	10,27	10,60	3,25	35,22
	CX 2789–2	303,4	9,29	8,93	–3,82	29,45	10,35	10,45	0,99	34,45
	CX 271–2	301,4	9,23	8,99	–2,53	29,84	10,28	10,70	4,08	35,51
	CX 89–2	307,7	9,42	8,97	–4,76	29,16	10,50	10,52	0,21	34,19
min.					–4,76				0,21	
max.					–2,47				4,08	
Range					–2,30				–3,87	
Average						29,51				34,79
Actual						30,62				34,12
Standard deviation						0,30				0,50
2 × Standard deviation						0,59				1,00

			2-Methylpentane				**3-Methylpentane**			
	Sample	**Sample vol. ml**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**
Batch 1	CX 532–2	305,6	10,24	10,21	–0,32	33,40	10,53	10,61	0,81	34,73
	CX 3230–2	292	9,79	9,69	–0,96	33,19	10,06	10,08	0,23	34,53
	CX 83–2	300,9	10,08	10,13	0,49	33,68	10,37	10,53	1,59	35,00
	CX 2789–2	303,4	10,17	10,06	–1,06	33,15	10,45	10,47	0,18	34,52
	CX 271–2	301,4	10,10	10,26	1,60	34,05	10,38	10,68	2,83	35,43
	CX 89–2	307,7	10,31	10,13	–1,72	32,93	10,60	10,52	–0,81	34,17
min.					–1,72				–0,81	
max.					1,60				2,83	
Range					–3,32				–3,64	
Average						33,40				34,73
Actual						33,51				34,45
Standard deviation						0,59				0,65
2 × Standard deviation						1,18				1,30

Table D.5 — Solvent desorption results (Test 2)

			Benzene				2,2-Dimethylbutane			
	Sample	**Sample vol. ml**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**
Batch 1	3862540066			< 1				< 1,0		
	3862540073			< 1				< 1,0		
	3862539646	3071,1	94,0	88	–6,41	28,65	104,8	110	4,99	35,82
	3862539647	3025,3	92,6	85	–8,23	28,10	103,2	110	6,58	36,36
	3862540380	3064,2	93,8	88	–6,20	28,72	104,5	110	5,22	35,90
	3862539649	3064,9	93,8	77	–17,94	25,12	104,6	98	–6,28	31,97
	3862539650	2994,8	91,7	87	–5,12	29,05	102,2	110	7,66	36,73
	3862539651	*2990,8*	*91,6*	*45*	*–50,86*	*15,05*	*102,0*	*57*	*–44,14*	*19,06*
min.					–17,94				–6,28	
max.					–5,12				7,66	
Range					–12,83				–13,94	
Average						27,93				35,36
Actual						30,62				34,12
Standard deviation						1,61				1,93
2 × Standard deviation						3,21				3,85

			2-Methylpentane				3-Methylpentane			
	Sample	**Sample vol. ml**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**
Batch 1	3862540066			< 1,0				< 1,0		
	3862540073			< 1,0				< 1,0		
	3862539646	3071,1	102,9	110	6,89	35,82	105,8	110	3,96	35,82
	3862539647	3025,3	101,4	100	–1,36	33,05	104,2	110	5,54	36,36
	3862540380	3064,2	102,7	110	7,13	35,90	105,6	110	4,20	35,90
	3862539649	3064,9	102,7	94	–8,48	30,67	105,6	99	–6,24	32,30
	3862539650	2994,8	100,4	110	9,61	36,73	103,2	110	6,61	36,73
	3862539651	*2990,8*	*100,2*	*54*	*–46,12*	*18,06*	*103,0*	*57*	*–44,68*	*19,06*
min.					–8,48				–6,24	
max.					9,61				6,61	
Range					–18,09				–12,86	
Average						34,43				35,42
Actual						33,51				34,45
Standard deviation						2,52				1,78
2 × Standard deviation						5,04				3,57

Table D.6 — Thermal desorption results (Test 2)

			Benzene				2,2-Dimethylbutane			
	Sample	**Sample vol. ml**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**
Batch 2	CX-25–9	297,1	9,02	8,95	–0,72	30,13	10,05	10,54	4,93	35,48
	CX-753–9	291,4	8,84	8,76	–0,96	30,05	9,85	10,36	5,16	35,56
	CX-160–9	300,7	9,12	8,64	–5,33	28,73	10,17	10,15	–0,18	33,75
	CX-1624	302,9	9,19	8,66	–5,80	28,58	10,24	10,15	–0,86	33,52
	CX-1679–9	299,9	9,10	8,77	–3,61	29,25	10,14	10,33	1,86	34,44
	CX-1688–9	307,6	9,33	9,00	–3,62	29,25	10,40	10,56	1,49	34,32
min.				8,64				10,15		
max.				9,00				10,56		
Range				0,36				0,41		
Average						29,33				34,51
Actual						30,62				33,81
Standard deviation						0,65				0,85
2 × Standard deviation						1,29				1,71

			2-Methylpentane				3-Methylpentane			
	Sample	**Sample vol. ml**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**
Batch 2	CX-25–9	297,1	9,87	10,11	2,47	34,03	10,14	10,53	3,81	35,45
	CX-753–9	291,4	9,68	9,95	2,84	34,16	9,95	10,37	4,19	35,58
	CX-160–9	300,7	9,99	9,77	–2,20	32,48	10,27	10,16	–1,05	33,79
	CX-1624	302,9	10,06	9,76	–3,02	32,21	10,34	10,16	–1,79	33,54
	CX-1679–9	299,9	9,96	9,93	–0,33	33,10	10,24	10,34	0,99	34,48
	CX-1688–9	307,6	10,22	10,18	–0,40	33,08	10,50	10,55	0,40	34,28
min.				9,76				10,15		
max.				10,18				10,56		
Range				0,42				0,41		
Average						33,18				34,52
Actual						33,21				34,15
Standard deviation						0,19				0,84
2 × Standard deviation						0,37				1,68

Table D.7 — Solvent desorption results (Test 2)

			Benzene				**2,2-Dimethylbutane**			
	Sample	**Sample vol. ml**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**
Batch 2	3862540067	3043,7	92,4	85	–7,97	27,93	102,9	110	6,88	36,14
	3862540068	3027,0	91,9	84	–8,55	27,75	102,4	110	7,47	36,34
	3862540069	3055,7	92,7	85	–8,33	27,82	103,3	110	6,46	36,00
	3862540070	3069,3	93,1	85	–8,74	27,69	103,8	110	5,99	35,84
	3862540071	2995,0	90,9	80	–11,97	26,71	101,3	100	–1,25	33,39
	3862540072	2953,6	89,6	79	–11,86	26,75	99,9	97	–2,87	32,84
min.					–11,97				–2,87	
max.					–7,97				7,47	
Range					4,01				10,35	
Average						27,44				35,09
Actual						30,34				33,81
Standard deviation						0,56				1,55
2 × Standard deviation						1,11				3,10

			2-Methylpentane				**3-Methylpentane**			
	Sample	**Sample vol. ml**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**	**Loaded µg**	**Measured µg**	**Diff. %**	**mg/m^3**
Batch 2	3862540067	3043,7	101,1	100	–1,08	32,85	103,9	110	5,84	36,14
	3862540068	3027,0	100,5	100	–0,53	33,04	103,4	110	6,42	36,34
	3862540069	3055,7	101,5	110	8,39	36,00	104,3	110	5,42	36,00
	3862540070	3069,3	101,9	100	–1,90	32,58	104,8	110	4,96	35,84
	3862540071	2995,0	99,5	98	–1,48	32,72	102,3	100	–2,22	33,39
	3862540072	2953,6	98,1	93	–5,20	31,49	100,9	97	–3,82	32,84
min.					–5,20				–3,82	
max.					8,39				6,42	
Range					13,58				10,25	
Average						33,11				35,1
Actual						33,21				34,15
Standard deviation						1,52				1,55
2 × Standard deviation						3,03				3,10

Conclusions from the second NPL study:

— Although this is a limited data set, there would appear to be good agreement between solvent extraction and thermal desorption methods.

— Decreasing the sampling flow rate on the charcoal tubes from 200 ml/min to 100 ml/min does not appear to affect the sampling efficiency.

D.3.4 Comparative studies of solvent extraction and thermal desorption methods

Study [22] involved 38 European laboratories studying up to 7 organic compounds prepared in a precise environmental chamber at concentrations between 1 ppm and 100 ppm and between 20 %RH and 80 %RH. Good performance and correlation was obtained between all methods except for diffusively sampled charcoal/CS_2 monitoring methods which are not relevant here. Key factors influencing performance were found to be:

a) For thermal desorption methods: laboratory experience (e.g. in sorbent selection)

b) And for actively sampled charcoal tubes + CS_2 extraction: %RH and analyte concentration

Investigation [23] studied 90 VOCs at low ppb levels and high humidity (62 % to 95 %) and understandably found better performance of the thermal desorption procedure, given the concentrations involved. Nevertheless, for those compounds that were above the detection limits for the solvent extraction, meaningful correlation was obtained in most cases.

D.3.5 Guidance from US EPA Method 18 for stack emission testing using TD and SE

US EPA Method 18 allows both thermal desorption and solvent extraction based sorbent tube methods to be applied to stack gas testing. Relevant extracts from the text include:

Section 8.2.4 ‘Adsorption tube procedure. Any commercially available adsorbent’ (i.e. TD-compatible or charcoal) ‘is allowed for the purposes of this method, as long as the recovery study criteria in Section 8.4.3 are met.’

Text from later in the same section also indicates that NIOSH procedures are allowed, which would predominantly include solvent extraction methods.

8.2.4.3 ‘Standards and Calibration. If using thermal desorption, obtain calibration gases using the procedures in Section 10.1. If using solvent extraction, prepare liquid standards in the desorption solvent.’

The US Environmental Protection Agency’s acceptance of both thermal desorption and solvent extraction methods in their primary industrial emission standard for VOCs (Method 18) would indicate the suitability and equivalence of both procedures.

D.3.6 Validation studies for existing TD-based standards for monitoring speciated organic vapours

The following thermal desorption-based standards cover validation of thermal desorption-based methods for monitoring speciated vapour-phase organics in a wide range of monitoring scenarios including; workplace air, indoor air, outdoor air and chemical emission from products and materials:

- EN 14662-1 [15]
- EN ISO 16017-1 [5]
- MDHS 72 and 80 [10; 11]
- ISO 16000-6 [14]
- US EPA Method TO-17 and Method 0031 [16; 18]

Relevant validation tests were extensive and included (for example in EN ISO 16017-1):

- Retention volumes and breakthrough volumes for multiple (>50) compounds covering multiple chemical types
- Analytical precision (repeatability and reproducibility)
- Effect of storage (up to 14 months)
- Effect of high humidity
- Analyte recovery
- Standard deviation
- Assessment of blank levels
- Summary of overall uncertainty, precision, bias and storage

Provided advice given in CEN/TS 13649 is followed (e.g. regarding inclusion of a particulate filter, if needed (A1), the requirement to make sure the flue gas is cooled to 40 °C or below before reaching the sorbent bed and the need to ensure liquid water is not allowed to condense inside the sorbent sampling tube (all of which steps are critical for both charcoal and TD-compatible sorbents)) there is no fundamental difference between the process of sampling stack gas onto TD tubes and any of the vapour-sampling applications covered in the scope of the standard methods listed. The range of vapour monitoring conditions evaluated in validating the above standards is far great than that evaluated in the existing EN 13649 validation study (see above).

Similar validation data are included in the UK Health and Safety Laboratory method for determining volatile organic vapours in workplace air using sorbent tubes and thermal desorption – MDHS 72. In this case analyte masses in the order of 10µg on tube were evaluated and the following aspects of method robustness were assessed:

- Precision
- Storage (5 months and 11 months)
- Retention volumes and breakthrough volumes for multiple compounds covering multiple chemical types
- Impact of humidity on retention volumes

D.3.7 National calibration and validation protocols

Extract from Irish EPA Method A4: ‘Organics by ATD’ as applied for monitoring speciated organics in flue gas in the Irish Republic:

Section A4.2: “The method is suitable for the determination of volatile organic compounds which can be quantitatively trapped on Tenax TA™ and Unicarb (previously Spherocarb) adsorbent materials and determined by Thermal desorption and Gas chromatographic - Mass spectrometry techniques.”

Table D.8 gives a listing of the substances for which the method has been satisfactorily validated along with the calibration range of the method.

Table D.8 — List of substances for which the method has been validated and calibration range

Compound	**Calibration Range (µg on the tube)**	**Compound**	**Calibration Range (µg on the tube)**
Acetone	0,99 – 988	Trichloroethylene	1,46 – 1464
2-Propanol	0,98 – 981	Tetrachloroethylene	1,62 – 1623
Dichloromethane	1,66 – 1656	Chlorobenzene	1,11 – 1107
Ethylacetate	1,13 – 1127	Cyclohexanone	0,95 – 947
Hexane	0,824 – 824		
Heptane	0,855 – 855	Benzene	0,18 – 176
Methyl-ethyl-ketone	1,01 – 1007	Carbon tetrachloride	0,32 – 319
Methyl-isobutyl-ketone	1,00 – 1001	Chloroform	0,3 – 297
		1,2-Dichlorobenzene	0,26 – 261
Toluene	0,87 – 867	Dichloromethane	0,265 – 265
m-/p-Xylene	1,73 – 1729		
o-Xylene	0,88 – 880		
Tetrahydrofuran	0,88 – 887		

D.3.8 Additional support for TD-based methods

- Interlaboratory comparisons of monitoring vapour-phase components using TD (10 laboratories) [24].
- The US EPA Method 0031. Albeit that the technology used in this method has now been superseded, it was based on sorbent tubes with subsequent thermal desorption.
- The UK Environment Agency method for speciated organics in landfill gas. Landfill gas frequently comprises high concentrations of CO_2, methane and other gases, with elevated temperatures and high humidity. Use of a validated TD method for this application shows that thermal desorption is compatible with complex and challenging gas-phase matrices.
- Further confirmation that thermal desorption methods perform well under high humidity conditions comes from the extensive range of purge-and-trap methods for volatiles in ground water and drinking water, e.g. US EPA Method 524.2 [25]. All such standards are based on thermal desorption and have been validated extensively.

Common practice: Many/most stack testing laboratories in the UK, Ireland and France prefer and apply thermal desorption-based monitoring technologies because of the improved and more reliable analyte recovery performance, better sensitivity, no requirement for a toxic solvent and no risk of solvent interference.

D.3.9 Validation data for charcoal/solvent extraction methods

1) Validation of the first edition of EN 13649

See above critique.

2) Comparative studies of charcoal/CS_2 and thermal desorption methods

See D.3.3 and D.3.4.

3) Experience with US EPA Method 18 for stack emission testing using TD and SE

See D.3.5.

4) Validation studies are referenced in various charcoal/CS_2 based standard methods including:

- EN 14662-2 [15]
- ISO 16200 [6]
- MDHS 88 and 96 [12; 13]
- NIOSH standards

Common practice: All stack testing laboratories in Germany prefer to apply charcoal/CS_2-based monitoring technologies because of their many years of successful application of this method and their confidence that it offers sufficient sensitivity to accommodate the minimum concentrations of interest at the current time.

D.3.10 Conclusions and recommendations

1) The original validation work carried out for EN 13649 using charcoal/CS2 procedures is not fit for purpose (see D.2).

2) While extensive validation data exists for the use of thermal desorption and charcoal/solvent extraction to monitor vapour-phase organics under a wide range of conditions (concentration, humidity), these tests have not been carried out on real stacks.

3) Provided advice given in CEN/TS 13649 is followed, for example regarding the required sampling probe components, the temperature at which the gas is allowed to reach the sorbent sampling surface and preventing the formation of liquid water within the sorbent tube there should be no fundamental difference between the matrix generated in a robust standard atmosphere chamber (e.g. CATFAC or VITO installation) and that reaching the sampling surface of the sorbent in a well constructed stack sampling probe.

4) There are a lot of precedents accepting equivalence of the two different modes of analyte extraction (TD and SE) in all other areas of vapour sampling (workplace, indoor, ambient) and both methods have been well validated for these other areas. The only difference between these two methods is the mode of extraction of the retained chemicals from the sorbent media. Other aspects including sampling probe requirements, sampling constraints and analytical method are the same.

5) If the committee feel that field data, including real industrial emission measurement, is required for both TD and SE approaches in order validate CEN/TS 13649, the task will not be insubstantial and will require some compromises. The range of applicable industrial emission processes and stack types is considerable and the sheer number of organic compounds of interest, as specified in current BREF guidance, makes it impractical to consider a comprehensive validation with all potential analytes of interest and all different types of stack. Representative examples will have to be selected that allow reasonably safe extrapolation to the full range of possible real world monitoring scenarios. Parameters to consider will include:

   a) Categories of industrial emission (stack) (wet/dry, gas composition, temperature, etc.)

   b) Which compounds of interest to select

   c) Which concentration range to study

   d) The number of participating laboratories required

   e) Parallel evaluation with both methods (and with an independent method?) using the sampling and analytical parameters specified in CEN/TS 13649

Annex E
(informative)

Safety measures

The ventilation should be sufficient to prevent the inhalation of solvent fumes (CS_2 toxicity) during solvent desorption of solid sorbent tubes. Gloves and safety glasses should be worn to prevent the solvent coming into contact with the skin or eyes. The gloves should be thick enough to prevent injury from a damaged carbon tube.

Attention should be given to the general working environment and any associated local safety instructions (including the possible need for proved explosive equipment).

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