



# SLOVENSKI STANDARD

## SIST-TS CEN/TS 13649:2015

01-februar-2015

Nadomešča:  
SIST EN 13649:2002

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**Emisije nepremičnih virov - Določevanje masne koncentracije posameznih organskih spojin v plinasti fazi - Vzorčenje z adsorpcijo in ekstrakcija s topilom ali termična desorpcija**

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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Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von gasförmigen organischen Einzelverbindungen - Sorptive Probennahme mit Lösemittelextraktion oder thermischer Desorption

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Emissions de sources fixes - Détermination de la concentration massique en composés organiques gazeux individuels - Echantillonnage par adsorption et désorption des solvants ou désorption thermique

**Ta slovenski standard je istoveten z: CEN/TS 13649:2014**

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**ICS:**

13.040.40      Emisije nepremičnih virov      Stationary source emissions

**SIST-TS CEN/TS 13649:2015**

**en,fr,de**

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TECHNICAL SPECIFICATION  
 SPÉCIFICATION TECHNIQUE  
 TECHNISCHE SPEZIFIKATION

**CEN/TS 13649**

December 2014

ICS 13.040.40

Supersedes EN 13649:2001

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

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**CEN/TS 13649:2014 (E)****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 ( $\text{mg}/\text{m}^3$ ) 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

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**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.

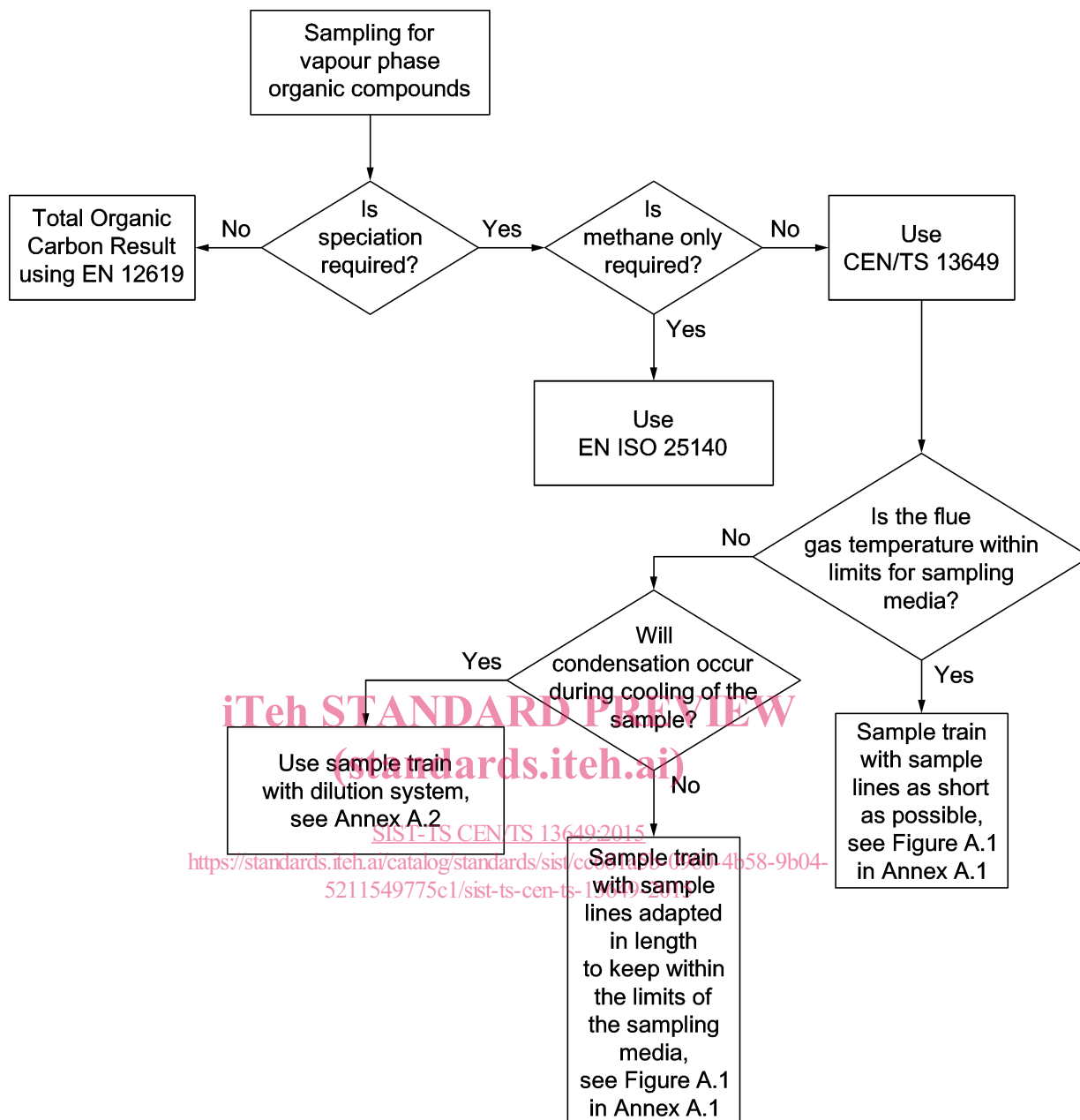
**5 Apparatus and materials****5.1 Method of measurement**

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  $\text{mg}/\text{m}^3$ , 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.

**CEN/TS 13649:2014 (E)****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.

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**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<sup>3</sup>, 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<sub>2</sub>) is a suitable extraction solvent for most of the compounds likely to be encountered in solvent using processes <https://standards.iteh.ai/catalog/standards/sist/cc681a5b-0960-4b58-9b04-5211549775c1/sist-ts-cen-ts-13649-2015>

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.

**CEN/TS 13649:2014 (E)****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.