SLOVENSKI STANDARD
oSIST prEN 13649:2011

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Emisije nepremičnih virov - Določevanje masne koncentracije posameznih organskih spojin v plinasti fazi - Metoda z aktivnim ogljem in desorpcije s topilom

Stationary source emissions - Determination of the mass concentration of individual gaseous organic compounds - Active carbon and solvent desorption method

Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von einzelnen gasförmigen organischen Verbindungen - Aktivkohleadsorptions- und Lösemitteldesorptionsverfahren

Emissions de sources fixes - Détermination de la concentration massique en composés organiques gazeux individuels - Méthode par charbon actif et désorption des solvants

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13.040.40	Emisije nepremičnih virov	Stationary source emissions

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English Version

Stationary source emissions - Determination of the mass concentration of individual gaseous organic compounds - Active carbon and solvent desorption method

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This draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 264.

If this draft becomes a European Standard, CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

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

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Contents

Foreword

This document (prEN 13649:2011) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

This document is currently submitted to the CEN Enquiry.

This document will supersede EN 13649:2011.

This European Standard has been prepared under a mandate given to CEN by the European Commission and European Free Trade Association.

The Annexes A, B, C are normative, D and E are informative.

1 Scope

This European Standard 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. It is a reference method.

The results obtained using this standard are expressed as the mass concentration (mg/m³) of the individual gaseous organic compounds. This Standard is suitable for measuring individual VOCs ranging in concentration from about 0,5 mg/m³ (solid adsorbent/solvent extraction methods) or from about 0,005 mg/m³ (thermal desorption methods). The upper range is defined by the method selected.

An alternative Method may be used provided that the user can demonstrate equivalence to this method according to the Technical Specification CEN/TS 14793, to the satisfaction of his national accreditation body or law.

This standard may be used to meet the monitoring requirements of applicable EC Directives.

This standard may be used for other organic compounds where validated.

This standard is not suitable for measuring total organic carbon (TOC). For the measurement of the mass concentration of total organic carbon then EN 12619 is applicable.

2 Normative references

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

EN15259, *Air quality — Measurement of stationary source emissions — Requirements for measurement sections and sites and for the measurement objective, plan and report*

EN14789, *Stationary source emissions — Determination of volume concentration of oxygen (O_2) — Reference method — Paramagnetism*

EN 14790, *Stationary source emissions — Determination of the water vapour in ducts*

ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

ISO 9169, *Air Quality — Determination of performance characteristics of measurement methods*

3 Terms and definitions

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

3.1
condensate trap
vessel designed to remove moisture from the sample waste gas

3.2
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

3.3
detection limit
minimum concentration of a compound which produces an observable response, as referred to in ISO 9169

3.4
dilution gas
gas used to dilute sampled waste gas to prevent water condensation

3.5
gaseous waste product
gaseous waste product from an industrial-scale process in which solvent or some other potentially toxic or odorous organic chemical vapour may be present Reference conditions

The limit values of EU Directives are expressed in mg/m³, on a wet basis, for non combustion process and on a dry bases, for combustion processes, at the reference conditions of 273 K and 101,3 kPa.

3.6
sampling tube for solvent extraction
commercially available glass tube filled with activated carbon or similar as the adsorbent

3.7
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

3.8
uncertainty
parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand

3.9
uncertainty budgets
calculation table combining all the sources of uncertainty according to ISO 14956 or ENV 13005 in order to calculate the overall uncertainty of the method at a specified value

3.10
overall uncertainty
expanded combined standard uncertainty attached to the measurement result calculated according to ENV 13005

3.11
VOC
definition from solvent directive:

Volatile organic compound (VOC) shall mean 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. For the purpose of this Directive, the fraction of creosote which exceeds this value of vapour pressure at 293,15 K shall be considered as a VOC;

4 Principle

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

Sampling approaches vary depending on waste gas conditions. Suitable capture medium must be selected. Solvent extraction or thermal desorption may be used. Analysis is by gas chromatography.

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 Council Directive 1999/13/EEC produce waste gases which do not have a high water content. Where high solvent concentrations or the condensation of water vapour is expected, this European Standard requires the use of dilution or condensate trap sampling system e.g. catchpot sampling systems (see Annex A). When condensate trap sampling systems are used then the condensate must be analysed.

Liquid water interferes with the sorption process and shall not be allowed to reach the sorbent material (activated carbon or thermal desorption compatible sorbents).

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

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

5.2 Sampling system

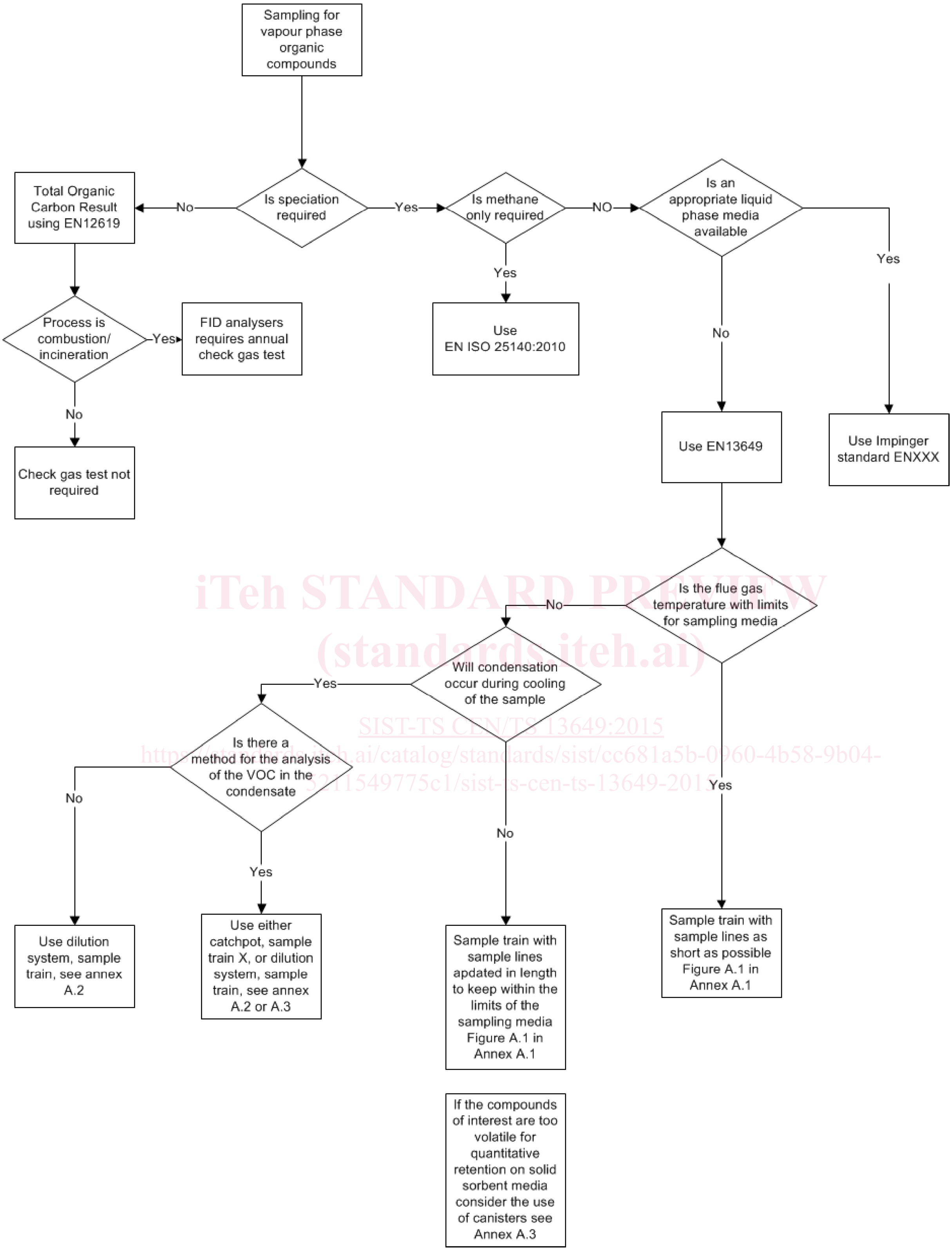

Figure 1 — Decision tree for determination of sampling procedure

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

All components of the sampling system shall be made of suitable inert material, i.e. must not interfere with the compound that is being determined. To avoid contamination from particulate a dust filter shall be provided.

Other methods of sampling can be used e.g. dilution or canister sampling, see Annex A.

NOTE Canisters are also predominantly used for 'grab' sampling not time weighted average monitoring (see Annex A).

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 not less than 100 mg of activated carbon;
- a security adsorbent layer to detect breakthrough, containing not less than 50 mg of activated carbon;

NOTE 1 Suitable types of tubes are NIOSH type B filled 100mg with activated carbon prepared from coconut shell and 50 mg in the security layer. For higher concentration then NIOSH Type G (750 mg main adsorbent layer, 250 mg security adsorbent layer) can be used.

- the sorbent tube construction material shall be inert.

NOTE 2 A suitable material is glass; the fresh tubes are closed by melted ends.

Sampling 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 e.g. 10 % of emission limit values

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.

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 B 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 B 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 must not damage tube ends.

NOTE 1 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).

NOTE 2 While thermal desorption sampling tubes can be re-used many times and while the process of thermal desorption inherently re-conditions the tubes during analysis, care must be taken to ensure that artefact levels do not interfere with measurement.

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 e.g. 10 % of emission limit values. See also 6.7.

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 100 ml/min for thermal desorption tubes or up to 1 l/min for charcoal tubes); typical flow rate and sample volume ranges for activated carbon and thermal desorption tubes are given in Annexes C and B 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/m³, 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 Annexes B and 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, if required for reporting at standard conditions, shall be less than ± 2,5 K and less than ± 1,0 % respectively.

5.6 Analytical reagents

5.6.1 General

Only reagents of recognised 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 1 Carbon disulphide (CS_2) is a suitable extraction solvent for most of the compounds likely to be encountered in solvent using processes.

NOTE 2 Beware of low and variable recovery rates for polar compounds, particularly from humid samples. 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.

NOTE 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 Section 7.1.2) or that can be chromatographically resolved from the compounds of interest during analysis.

In both cases (liquid extraction and thermal desorption), the range between the lowest and highest level standard shall be at least a factor of 20.

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 whilst 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 automatic sample tube loading, 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 B).

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 providing it is representative of the compound of interest.

6.2 Sampling time, volume and flow rate

The test laboratory shall have a documented procedure, to describe how to determine an appropriate sampling volume and time. 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 and the breakthrough volume or capacity of the tube for the compounds concerned.

NOTE 1 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 thermal desorption and charcoal tubes are described in Annexes B and 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.

NOTE 2 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 shall be minimised. In the case of monitoring steady-state emissions with thermal desorption tubes this can be achieved using simple grab-sampling apparatus (see Section 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 shall be used to maintain sampling flow rates and volumes at an accurate level while minimising risk of sample overload and breakthrough. Dilution can be either static or dynamic (see Annex B).

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 for more information. Maximum breakthrough allowed shall be less than 5 % of the overall concentration (see 9).

NOTE 3 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.

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 before and after sampling.

6.5 Handling, storage, transport of sampled tubes

6.5.1 General

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

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 20 °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 (Subclause 6.2). 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 20 °C.

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