



SLOVENSKI STANDARD

SIST EN 14662-4:2005

01-september-2005

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Ambient air quality - Standard method for measurement of benzene concentrations - Part 4: Diffusive sampling followed by thermal desorption and gas chromatography

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Außenluftbeschaffenheit - Standardverfahren zur Bestimmung von Benzolkonzentrationen - Teil 4: Diffusionsprobenahme mit anschließender Thermodesorption und Gaschromatographie

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Qualité de l'air ambiant - Méthode normalisée pour le mesurage de la concentration en benzène - Partie 4: Prélèvement par diffusion suivi d'une désorption thermique et d'une analyse par chromatographie en phase gazeuse

Ta slovenski standard je istoveten z: EN 14662-4:2005

ICS:

13.040.20 Kakovost okoljskega zraka Ambient atmospheres

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EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 14662-4

May 2005

ICS 13.040.20

English version

**Ambient air quality - Standard method for measurement of
benzene concentrations - Part 4: Diffusive sampling followed by
thermal desorption and gas chromatography**

Qualité de l'air ambiant - Méthode pour le mesurage des
concentrations en benzène - Partie 4 - Echantillonnage par
diffusion suivi d'une désorption thermique et d'une
chromatographie en phase gazeuse

Luftbeschaffenheit - Standardverfahren zur Bestimmung
von Benzolkonzentrationen - Teil 4: Diffusionsprobenahme
mit anschließender Thermodesorption und
Gaschromatographie

This European Standard was approved by CEN on 21 March 2005.

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This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

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Foreword

This European Standard (EN 14662-4:2005) has been prepared by Technical Committee CEN/TC 264 "Air Quality", the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by November 2005, and conflicting national standards shall be withdrawn at the latest by November 2005.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive 2000/69/EC and EU Directive 96/62 EC.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

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EN 14662-4:2005 (E)**1 Scope**

This part of EN 14662 is in accordance with the generic methodology selected as the basis of the European Union for the determination of benzene in ambient air [1] for the purpose of comparison of measurement results with limit values with a one-year reference period.

This part of EN 14662 gives general guidance for the sampling and analysis of benzene in air by diffusive sampling, thermal desorption and capillary gas chromatography.

This part of EN 14662 is valid for the measurement of benzene in a concentration range of approximately 0,5 $\mu\text{g}/\text{m}^3$ to 50 $\mu\text{g}/\text{m}^3$ in an air sample typically collected over a period of 14 days.

The upper limit of the useful range is set by the sorptive capacity of the sorbent and by the linear dynamic range of the gas chromatograph column and detector or by the sample splitting capability of the analytical instrumentation used. The lower limit of the useful range depends on the noise level of the detector and on blank levels of benzene and/or interfering artefacts on the sorbent. Artefacts are typically sub ng for sorbents such as graphitised carbon, but higher levels of aromatic hydrocarbons have been noted in other sorbents.

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.

ENV 13005:1999, *Guide to the expression of uncertainty in measurement*

EN 13528-2:2002, *Ambient air quality - Diffusive samplers for the determination of concentrations of gases and vapours - Requirements and test methods. Part 2: Specific requirements and test methods*

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EN 13528-3:2003, *Ambient air quality - Diffusive samplers for the determination of concentrations of gases and vapours - Requirements and test methods - Part 3: Guide to selection, use and maintenance*

EN ISO 16017-2, *Indoor, ambient and workplace air – Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography – Part 2: Diffusive sampling (ISO 16071-2:2003)*

EN ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories* (ISO/IEC 17025:1999)

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results - Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

ISO 5725-3:1995, *Accuracy (trueness and precision) of measurement methods and results - Part 3: Intermediate measures of the precision of a standard measurement method*

3 Terms and definitions

For the purposes of this European Standard, the following definitions apply.

NOTE: Attention is drawn to the fact that the terms *Ambient Air* and *Limit Value* are defined in Directive 96/62/EC [2].

3.1

certified reference material

A reference material [3.7], accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes its traceability to an accurate realisation of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence.

[ISO Guide 30:1992]

3.2

combined standard uncertainty

Standard uncertainty of the result of a measurement when that result is obtained from the values of a number of other quantities, equal to the positive square root of a sum of terms, the terms being the variances or covariances of these other quantities weighted according to how the measurement result varies with changes in these quantities

[ENV 13005:1999]

3.3

desorption efficiency

Ratio of the mass of analyte desorbed from a sampling device to that applied

[EN 838:1995]

3.4

diffusive sampler

A device which is capable of taking samples of gases or vapours from the atmosphere at a rate controlled by a physical process such as gaseous diffusion through a static air layer or a porous material and/or permeation through a membrane, but which does not involve the active movement of air through the device

[EN 13528-1]

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NOTE 1 Active normally refers to the pumped movement of air.

NOTE 2 This definition differs from that in EN 838:1995 by the addition of the words "or a porous material".

3.5

diffusive uptake rate

The rate at which the diffusive sampler collects a particular gas or vapour from the atmosphere, expressed in picograms per parts per billion¹ per minute (pg/ppb/min) or cubic centimetres per minute (cm³/min)

NOTE 1 pg/ppb/min are equivalent to ng/ppm/min.

NOTE 2 This definition differs from that in EN 838:1995 by the substitution of "picograms per parts per billion" for "nanograms per parts per million". The expression is numerically the same, but ambient concentrations are usually in the ppb range.

3.6

expanded uncertainty

Quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand

[ENV 13005:1999]

NOTE 1 The fraction may be viewed as the coverage probability or level of confidence of the interval.

¹ ppb is volume fraction, (φ)=10⁻⁹; ppm is volume fraction, (φ)=10⁻⁶.

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NOTE 2 To associate a specific level of confidence with the interval defined by the expanded uncertainty requires explicit of implicit assumptions regarding the probability distribution characterised by the measurement result and its combined standard uncertainty. The level of confidence that can be attributed to the interval can be known only to the extent to which such assumptions may be justified.

NOTE 3 Expanded uncertainty is termed *overall uncertainty* in ENV 13005:1999.

3.7**reference material**

A material or substance, one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.

[ISO Guide 30:1992]

3.8**repeatability conditions**

Conditions where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time

[ISO 3534-1:1993]

3.9**standard uncertainty**

Uncertainty of the result of a measurement expressed as a standard deviation

[ENV 13005:1999]

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3.10**uncertainty (of measurement)**

Parameter, associated with the results of a measurement, that characterises the dispersion of values that could reasonably be attributed to the measurand

NOTE 1 The parameter may be, for example, a standard deviation (or given multiple of it), or the half width of an interval having a stated level of confidence.

NOTE 2 Uncertainty of measurement comprises, in general, many components. Some of these components may be evaluated from the statistical distribution of the results of a series of measurements and can be characterised by experimental standard deviations. The other components, which can also be characterised by standard deviations, are evaluated from assumed probability distributions based on experience or other information.

NOTE 3 It is understood that the result of a measurement is the best estimate of the value of a measurand, and that all components of uncertainty, including those arising from systematic effects, such as components associated with corrections and reference standards, contribute to this dispersion [ENV 13005:1999].

4 Method description**4.1 Principle**

The diffusive sampler is exposed to air for a measured time period. [EN ISO 16017-2]. The rate of sampling is determined by prior calibration in a standard atmosphere (4.2.5) The benzene vapour migrates down the tube by diffusion and is collected on the sorbent. The collected vapour (on each tube) is desorbed by heat and is transferred under inert carrier gas into a gas chromatograph equipped with a capillary column and a flame ionization detector or other suitable detector, where it is analysed. The analysis is calibrated by means of liquid or vapour spiking onto a sorbent tube or from comparative field trials.

Information on possible saturation of the sorbent bed, the effect of transients and the effect of face velocity is given in EN 13528-3. This also explains the dependence of diffusion uptake rates on the concentration level

of pollutants and the time of diffusive sampling, for non-ideal sorbents, which results in different values being given in Annex A. The theory of performance of diffusive samplers is also given in EN 13528-3.

4.2 Reagents and materials

During the analysis, use only reagents of recognised analytical reagent grade.

Use only volumetric glassware and syringes that are calibrated to ensure traceability of volume to primary standards.

4.2.1 Benzene

Benzene is required as a reagent for calibration purposes, using either liquid spiking (4.2.7) or vapour spiking (4.2.6) onto sorbent tubes.

4.2.2 Dilution solvent

A dilution solvent is required for preparing calibration blend solution for liquid spiking (4.2.7). This should be of chromatographic quality. It shall be free from compounds co-eluting with benzene.

NOTE Methanol is frequently used. Alternative solvents may be used provided they do not interfere with the gas chromatographic analysis, either by co-elution or by altering detector response.

4.2.3 Sorbents

A particle size 0,18 mm to 0,25 mm (60 to 80 mesh) is recommended. Sorbent particle sizes larger than 0,18 to 0,25 mm may be used. Smaller sorbent particle size ranges are not recommended because of back pressure problems. Each sorbent should be preconditioned under a flow of inert gas by heating it at a temperature at least 25 °C below the published maximum for that sorbent overnight before packing the tubes. To prevent recontamination of the sorbents, they shall be kept in a clean atmosphere during cooling to room temperature, storage, and loading into the tubes. Wherever possible, analytical desorption temperatures should be kept below those used for conditioning. Tubes prepacked by the manufacturer are also available for most sorbents and as such only require conditioning.

NOTE A description of sorbents is given in Annex B and a guide for sorbent selection is given in Annex C. Equivalent sorbents may be used. A guide to sorbent conditioning and analytical desorption parameters is given in Annex D.

4.2.4 Calibration standards

Calibration standards are preferably prepared by sampling a known volume from standard atmospheres (4.2.6) as this procedure most closely resembles the practical sampling situation.

If this way of preparation is not practicable, standards may be prepared by a liquid spiking procedure (4.2.7, 4.2.8) provided that the accuracy of the spiking technique is either:

- a) established by using procedures giving spiking levels fully traceable to primary standards of mass and/or volume, or,
- b) confirmed by comparison with certified reference materials if available, standards produced using standard atmospheres, or results of reference measurement procedures.

To minimise matrix effects calibration tubes should be closely matched to the sample tubes with respect to sorbent type, particle size and mass.

EN 14662-4:2005 (E)**4.2.5 Standard atmospheres**

Prepare standard atmospheres of known concentrations of benzene by a recognised procedure. Methods described in ISO 6144 and ISO 6145 are suitable. If the procedure is not applied under conditions that will allow the establishment of full traceability of the generated concentrations to primary standards of mass and/or volume the concentrations need to be confirmed using an independent procedure.

4.2.6 Standard sorbent tubes loaded from standard atmospheres

Prepare loaded sorbent tubes by passing an accurately known volume of the standard atmosphere through the sorbent tube e.g. by means of a pump. The volume of atmosphere sampled shall not exceed the breakthrough volume of the sorbent. After loading the tube is disconnected and sealed. Prepare fresh standards representing benzene levels in the samples corresponding to the concentration range of $0,5 \mu\text{g}/\text{m}^3$ to $50 \mu\text{g}/\text{m}^3$ with each batch of samples, or use spiked control samples to determine consistency of detector response.

4.2.7 Preparation of standard solutions for liquid spiking, gravimetric procedure.**4.2.7.1 Solution containing approximately 10 mg/ml benzene**

Weigh a 100 ml volumetric flask and introduce approximately 75 ml of dilution solvent. Then accurately weigh approximately 1 g benzene into the flask. Make up to 100 ml with dilution solvent, stopper or cap, weigh and shake to mix.

4.2.7.2 Solution containing approximately 100 $\mu\text{g}/\text{ml}$ benzene

Weigh a 100 ml volumetric flask and introduce approximately 75 ml of dilution solvent. Then accurately weigh approximately 1 ml of solution described in 4.2.7.1 into the flask. Make up to 100 ml with dilution solvent, stopper or cap, weigh and shake to mix

4.2.7.3 Solution containing approximately 50 $\mu\text{g}/\text{ml}$ benzene

Introduce 30 ml of dilution solvent into a preweighed 100 ml volumetric flask. Weigh in 50 ml of solution described in 4.2.7.2. Make up to 100 ml with dilution solvent, stopper or cap, weigh and shake to mix.

4.2.7.4 Solution containing approximately 10 $\mu\text{g}/\text{ml}$ benzene

Introduce 50 ml of dilution solvent into a preweighed 100 ml volumetric flask. Weigh in 10 ml of solution described in 4.2.7.2. Make up to 100 ml with dilution solvent, stopper or cap, weigh and shake to mix

4.2.7.5 Solution containing approximately 5 $\mu\text{g}/\text{ml}$ benzene

Introduce 50 ml of dilution solvent into a preweighed 100 ml volumetric flask. Weigh in 5 ml of solution described in 4.2.7.2. Make up to 100 ml with dilution solvent, stopper or cap, weigh and shake to mix.

4.2.7.6 Solution containing approximately 1 $\mu\text{g}/\text{ml}$ benzene

Introduce 50 ml of dilution solvent into a preweighed 100 ml volumetric flask. Weigh in 1 ml of solution described in 4.2.7.2. Make up to 100 ml with dilution solvent, stopper or cap, weigh and shake to mix.

4.2.8 Preparation of standard solutions for liquid spiking, volumetric procedure

Alternatively, calibration solutions may be prepared by serial dilution of a stock solution of benzene in a dilution solvent using volumetric glassware and syringes that are traceably calibrated. The calibration may be performed by repeated weighing of the corresponding volume of water, using the appropriate specific density to calculate the volume of the glassware. When preparing solutions in carbon disulphide by volumetry the

temperature in the working room shall be controlled to within ± 2 K in order to limit the effect of variations of the specific density of the dilution solvent.

The dilution steps described in clause 4.2.7 may be used to prepare calibration standard solutions in the appropriate benzene concentration range, using calibrated flasks, vials, syringes and pipettes.

4.2.9 Stability of standard solutions

Fresh standard solutions should be prepared weekly, or more frequently if evidence is noted of deterioration.

4.2.10 Standard sorbent tubes loaded by liquid spiking

Loaded sorbent tubes are prepared by injecting aliquots of standard solutions onto clean sorbent tubes as follows. A sorbent tube is fitted to a T piece of which one end is fitted with a septum, or injection facility of a gas chromatograph through which inert purge gas is passed at 100 ml/min. Inject an aliquot of an appropriate standard solution through the septum and purge for 5 minutes. The tube is then disconnected and sealed. Prepare fresh standards with each batch of samples, or use spiked control samples to determine consistency of detector response.

NOTE In the case of methanol, a 5 μ l aliquot, a purge gas flow of 100 ml/min and a 5 min purge time have been found to be appropriate to eliminate most of the solution solvent from the tube if packed with Tenax. If other dilution solvents and sorbents are used, the conditions should be determined experimentally.

NOTE A conventional gas chromatographic injection port may be used for preparing sample tube standards. This can be used in situ, or it can be mounted separately. The carrier gas line to the injector should be retained. The back of the injection port should be adapted if necessary to fit the sample tube. This can be done conveniently by means of a compression coupling with a O-ring seal.

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4.3 Apparatus

The following specific items of laboratory apparatus are required.

4.3.1 Sorbent tubes

These tubes shall be compatible with the thermal desorption apparatus to be used (4.3.8). Typically, they are constructed of stainless steel tubing, 6,4 mm (1/4 inch) OD, 5 mm ID and 90 mm long. Tubes of other dimensions may be used but the uptake rates given in Annex A are based on these tube dimensions. One end of the tube is marked, for example by a scored ring about 10 mm from the (diffusion) sampling end. The tubes are packed with preconditioned sorbents so that the sorbent bed will be within the desorber heated zone and a consistent gap of about 14 mm is retained at the marked (diffusion) end of the tube, when measured with the diffusion cap removed.

NOTE Uptake rates in Annex A are given for tubes with a nominal air gap (between sorbent bed and diffusion end cap) of 15 mm. In practice, packed tube dimensions will vary and tubes should be rejected where the air gap (between stainless steel screen retaining the sorbent bed and the end of the tube) is outside the range 14,0 mm to 14,6 mm, when measured with the diffusion cap removed.

Tubes contain between 200 mg and 1000 mg sorbent, depending on sorbent density - typically about 250 mg porous polymer, or 500 mg carbon molecular sieve or graphitised carbon. The sorbents are retained by a stainless steel gauze at the diffusion end and an unsilanised glass wool plug and/or a second stainless gauze at the other

4.3.2 Sorbent tube end caps

The tubes shall be sealed to prevent significant contamination, e. g. with metal screw cap fittings with PTFE ferrules.

EN 14662-4:2005 (E)**4.3.3 Diffusion end caps**

The diffusion end cap is similar to 4.3.2, but allows the ingress of vapour through a metal gauze, the size of the opening being the same as the cross-section of the tube.

Some versions of the end cap incorporate a silicone membrane next to the gauze.

4.3.4 Syringes

A precision 10 µl liquid syringe readable to 0,1 µl. The volume of the liquid delivered by the syringe shall be calibrated by gravimetry.

4.3.5 Precipitation shield

A protective cover to prevent the entrance of particles or water droplets into the sampling tube during the sampling.

NOTE EN 13528-3 describes various shields for diffusive samplers.

4.3.6 Support

A device capable of positioning the sorbent tube at the appropriate height and distance from obstacles to warrant undisturbed sampling.

4.3.7 Gas chromatograph

A gas chromatograph fitted with a flame ionization, photo ionization, mass spectrometric or other suitable detector, capable of detecting an injection of 1 ng benzene with a signal-to-noise ratio of at least 10:1.

A gas chromatograph column capable of separating benzene from other components.

4.3.8 Thermal desorption apparatus

Apparatus for the two-stage thermal desorption of the sorbent tubes and transfer of the desorbed vapour via an inert gas flow into a gas chromatograph shall be required. 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, and a cold trap in the transfer line to concentrate the desorbed sample (4.6.2). The desorbed sample, contained in the purge gas, is routed to the gas chromatograph and capillary column via a heated transfer line.

4.4 Sample tube conditioning

Prior to use, tubes shall be conditioned by desorbing them at a temperature at or just above the analytical desorption temperature (see Annex D). Typical conditioning time is 10 min with a carrier gas flow of at least 100 ml/min. The carrier gas flow should be in a direction opposite to that used during sampling. Tubes should then be analysed, using routine analytical parameters, to ensure that the thermal desorption blank is sufficiently small. If the blank is unacceptable, tubes should be reconditioned by repeating this procedure. Once a sample has been analysed, the tube may be reused to collect a further sample immediately. However, it is advisable to check thermal desorption blank if the tubes are left for an extended period before reuse, or if sampling for a different analyte is envisaged. Tubes should be sealed with metal screw caps with combined PTFE ferrule fittings and stored in an airtight container when not sampling or being conditioned.

4.5 Sampling

Select a sorbent tube (or tubes) appropriate for sampling benzene. Guidance on suitable sorbents is given in Annex C.