SLOVENSKI STANDARD
SIST EN 14662-2:2005

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Kakovost zunanjega zraka - Standardna metoda za doloļ evanje koncentracije benzena - 2. del: Vzorļ enje s ļ rpanjem in doloļ evanje s plinsko kromatografijo po desorpciji v topilu

Ambient air quality - Standard method for measurement of benzene concentrations - Part 2 : Pumped sampling followed by solvent desorption and gas chromatography

Luftbeschaffenheit - Standardverfahren zur Messung von Benzolkonzentrationen - Teil 2: Probenahme mit einer Pumpe mit anschließender Lösemitteldesorption und Gaschromatographie

Qualité de l'air ambiant - Méthode normalisée pour le mesurage de la concentration en benzene - Partie 2 : Prélevement par pompage suivi d'une désorption au solvant et d'une analyse par chromatographie en phase gazeuse

Ta slovenski standard je istoveten z: **EN 14662-2:2005**

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13.040.20	Kakovost okoljskega zraka	Ambient atmospheres

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English version

Ambient air quality - Standard method for measurement of benzene concentrations - Part 2 : Pumped sampling followed by solvent desorption and gas chromatography

Qualité de l'air ambiant - Méthode pour le mesurage des concentrations en benzène - Partie 2 : Echantillonnage par pompage suivi d'une désorption au solvant et d'une chromatographie en phase gazeuse

Luftbeschaffenheit - Standardverfahren zur Messung von Benzolkonzentrationen - Teil 2: Probenahme mit einer Pumpe mit anschließender Lösemitteldesorption und Gaschromatographie

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

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Foreword

This European Standard (EN 14662-2:2005) 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of an identical text or by endorsement, at the latest by November 2005, and conflicting national standards shall be withdrawn at the latest by November 2005.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.

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1 Scope

This part of EN 14662 is in accordance with the generic methodology 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 pumped sampling, solvent 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 $\mu g/m^3$ to 50 $\mu g/m^3$ in an air sample of 1 m^3 volume, typically collected over a period of 24 hours.

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 and in the desorption solvent.

The method described here is based on sampling on sample tubes typically containing 100 mg of activated charcoal and desorption using carbon disulphide.

Alternative sorbents to activated charcoal may be used provided that the equivalence in performance characteristics of the procedure is demonstrated.

Alternative desorption solvents to carbon disulphide may be used provided that the equivalence in performance characteristics of the procedure is demonstrated.

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, *Guide to the expression of uncertainty in measurement*

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

ISO 6144, *Gas analysis – Preparation of calibration gas mixtures – Static volumetric method*

ISO 6145, *Gas analysis – Preparation of calibration gas mixtures using dynamic volumetric methods*

3 Terms and definitions

For the purposes of this European standard the following terms and 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 [3.5], 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 1076:1997]

3.4

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.

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.

3.5

Reference material

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

[ISO Guide 30:1992]

3.6

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]

3.7

Sampling efficiency

Ratio of the mass of analyte collected by a sampling device to that applied.

3.8

Standard uncertainty

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

[ENV 13005:1999]

3.9

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

A measured volume of sample air is drawn through an activated charcoal sorbent tube. Provided suitable sampling conditions are chosen, benzene is retained by the sorbent and thus is removed from the flowing air stream. The collected vapour is desorbed using carbon disulphide and is analyzed on a gas chromatograph equipped with a capillary column and a flame ionisation detector or other suitable detector. The analysis is calibrated by means of charcoal tube calibration standards or calibration solutions of known amounts of benzene in carbon disulphide.

4.2 Reagents and Materials

During the analysis, use only reagents of known purity appropriate to the application.

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 and for the determination of desorption efficiency.The benzene used shall be of a minimum established purity of 99,5%.

4.2.2 Carbon disulphide

The carbon disulphide used for the desorption of benzene from the charcoal shall be free from compounds interfering with the analysis of the benzene sampled.

Grades of carbon disulphide used shall contain benzene in concentrations less than 0,1 µg/ml.

4.2.3 Internal standard

An internal standard may be used to correct for small variations in the volume of carbon disulphide injected. It shall not interfere with benzene and it shall not be removed from the elution solvent by the charcoal. The internal standard shall contain less than 0,1 % benzene. The internal standard is added to the carbon disulphide before the preparation of calibration solutions (4.2.8) or the desorption of samples (4.6) or calibration standards (4.2.5).

Internal standards used in practice include 2-fluorotoluene (flame-ionization detection; photo-ionization detection) and benzene-d6 and toluene-d8 (mass-spectrometric detection).

4.2.4 Activated charcoal

A particle size of 0,35 mm to 0,85 mm is recommended. Before use, the charcoal shall be heated in an inert atmosphere, e.g. high-purity nitrogen, at approximately 600 °C for 1 hour. To prevent recontamination of the charcoal, it shall be kept in a clean atmosphere during cooling to room temperature, storage, and loading into the tubes. Tubes prepacked by manufacturers with pre-conditioned charcoal are also available and require no further conditioning.

NOTE The sorptive capacity and desorption efficiency of different batches of activated charcoal may vary. Commercial tubes, if used, should be purchased from the same batch and in sufficient number to provide consistent performance for a definite period of time.

4.2.5 Calibration standards

Calibration standards can be prepared by loading the required amounts of benzene from standard atmospheres (4.2.6) on charcoal tubes of the same batch as those used for sampling as this procedure most closely resembles the practical sampling situation.

The concentrations of the desorbed solutions of the sample tubes may then be compared directly with the solutions resulting from desorption of these tube standards, i.e., without the need for applying corrections for desorption efficiency (4.6.5).

If it is not practical to prepare calibration standards in this way, then calibration solutions in carbon disulphide can be prepared (see 4.2.8) in order to compare the concentrations of desorbed solutions (4.6.2) with those calibration standards in the gas chromatographic analysis.

In this case, appropriate corrections for desorption efficiency shall be applied (see 4.6.5).

NOTE The use of an internal standard as a surrogate to correct for desorption efficiency is not allowed. Desorption efficiency should be determined directly with benzene.

4.2.6 Standard atmospheres

Prepare standard atmospheres of known concentrations of benzene by a recognized 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 or if the chemical inertness of the generation system cannot be guaranteed, the concentrations need to be confirmed using an independent procedure.

4.2.7 Standard charcoal tubes loaded by spiking from standard atmospheres

Prepare loaded charcoal tubes by passing an accurately known volume of the standard atmosphere through the sorbent tube, e.g., by means of a mass-flow controller or a pump. After loading, the tubes are disconnected and sealed.

EXAMPLE

Prepare standard atmospheres with benzene concentrations in the range of 0,5 mg/m^3 to 50 mg/m^3. Prepare charcoal tube standards at a minimum of 5 levels corresponding to a range of 0,5 µg to 50 µg by sampling 100 ml to 1 l of these standard atmospheres.

NOTE The loading ranges given are not mandatory and approximate to the application range given in the scope for a 1 m^3 sample. For specific applications where other volumes are used and/or the concentration range of benzene is limited other loading ranges may be more appropriate.

Prepare fresh standards at appropriate intervals depending upon their stability.

Standards containing approximately 5 µg of benzene are known to be stable for at least 1 year when stored in a clean environment at room temperature [3].

4.2.8 Preparation of calibration solutions in carbon disulphide

4.2.8.1 General

Prepare a series (5 at minimum) of calibration solutions of benzene in carbon disulphide in the range corresponding to ambient concentrations of 0,5 µg/m^3 to 50 µg/m^3 of benzene. Guidance for the preparation of such solutions can be found in [4]. In general, procedures based on gravimetry and volumetry may be used to prepare calibration solutions under the conditions described below.

4.2.8.2 Gravimetric procedure

By preparing serial dilutions of benzene (4.2.1) in carbon disulphide (4.2.2) by weighing, the traceability of the composition of the final calibration standards is ensured. A suitable mass of internal standard (4.2.3) may be added to the carbon disulphide to correct for small evaporation losses of carbon disulphide or variations in the injected volume of carbon disulphide on analysis. The concentrations of benzene in the standard solutions are then expressed as mass fractions. By weighing the mass of carbon disulphide used for desorption of samples, blanks or standards for the determination of desorption efficiency (4.6.2) the analysis will yield the mass of benzene in the sample, blank or standard.

EXAMPLE

Accurately weigh approximately 100 mg of benzene into a 10 ml volumetric flask or vial using a balance with a resolution ≤ 0,1 mg. Make up to 10 ml with carbon disulphide (4.2.2), stopper or cap, weigh and shake to mix.

From this stock solution calibration standards may be prepared in the range of 100 µg/ml to 1000 µg/ml of benzene by pipetting 0,1 ml to 1 ml into 10 ml volumetric flasks or vials, capping, weighing, and subsequent addition of a known mass of carbon disulphide corresponding to approximately 10 ml.

From these solutions calibration standards in the range of 1 µg/ml to 50 µg/ml of benzene are prepared as above. The standard solution of 50 µg/ml is used to prepare the calibration standard containing 0,5 µg/ml of benzene.

NOTE In order to ensure an uncertainty of the final mass fractions of benzene appropriate to the application the uncertainty of the weighing equipment used (k=2) should be less than ± 0,1 mg.

4.2.8.3 Volumetric procedure

Alternatively, calibration solutions may be prepared by serial dilution of a stock solution of benzene in carbon disulphide 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. A suitable mass of internal standard (4.2.3) may be added to the carbon disulphide to correct for small evaporation losses of carbon disulphide or variations in the injected volume of carbon disulphide on analysis. 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 carbon disulphide.

The dilution steps described in the above example (4.2.8.2) 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 calibration solutions

Stock solutions are stable for at least one month when stored in dark glass flasks or vials with suitable caps at room temperature.

Typically, calibration solutions with concentrations between 0,5 µg/ml and 50 µg/ml should be prepared fresh weekly, or more frequently if evidence is noted of deterioration.

4.2.10 Standards for desorption efficiency

Prepare loaded sorbent tubes from standard atmospheres (4.2.6) according to the procedure described in 4.2.7.

If the generation of standard atmospheres is not practicable, the standards may be prepared by a liquid spiking procedure, provided that the accuracy of the spiking technique is established by using procedures giving spiking levels traceable to primary standards of mass and/or volume, or is confirmed by an independent procedure.

Load the sorbent tubes by injecting aliquots of standard solutions (4.2.8) of accurately known mass or volume 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 a known mass or volume through the septum and purge for 5 minutes. Disconnect the tube and seal.

4.3 Apparatus

The following specific items of laboratory equipment are required.

4.3.1 Sorbent tubes

A typical sampling tube consists of a glass tube with both ends flame-sealed, 70 mm long with an outside diameter of 6 mm and an inside diameter of 4 mm, containing two sections of sorbent. In the case of charcoal, the sorbing section contains 100 mg of charcoal and the back-up section, 50 mg. The sections are separated and their contents are held in place with an inert material, e.g. glass wool plugs (preferably silanized).

Glass tubes shall be held in protective holders to prevent breakage.

The desorption efficiency (*D*) for each batch of tubes shall be checked by one of the methods described in 4.6.5. If *D* is lower than 0,9 (90%), the tubes shall not be used.

NOTE 1 Instead of commercial two-section tubes, single section tubes may be used. This arrangement has the advantage that it is not necessary to store tubes at sub-ambient temperatures after sampling to prevent migration of the sorbed compounds from one section to the other.

NOTE 2 Tubes meeting these requirements are commercially available; however, they may also be made by the user. Self-packed samplers should not be used unless they can be shown to have reproducible and constant sorption properties.

4.3.2 End caps

Caps made of a suitable material to fit over the sorbent tubes (4.3.1) to prevent leakage.

NOTE Commercially available tubes are supplied with polyethylene end caps.

4.3.3 Syringes

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

4.3.4 Volumetric flask

Precision volumetric flasks of an accurately known volume, to be used for the preparation of calibration solutions (4.2.8). These should be obtained from suppliers issuing certificates of calibration traceable to internationally accepted standards or be traceably calibrated in the laboratory by weighing of water.

4.3.5 Sampling device

Sampling device capable of maintaining a preset flow rate of 500 ml/min to 1000 ml/min within ±5% during the required sampling period (typically 24 hours). As such, the following devices may be used:

- pump with an adjustable flow rate
- vacuum pump with a critical orifice
- vacuum pump with a mass-flow controller

- vacuum pump with a constant pressure drop over a restriction.

NOTE The sampling device should be in accordance with local safety regulations, if any.

4.3.6 Tubing

Tubing of appropriate length and internal diameter to ensure a leak-proof fit to both pump and sample tube or tube holder, if used.

4.3.7 Flow calibration device

A flow meter that is traceably calibrated to a primary flow standard over the desired flow range (4.3.5). The uncertainty in the calibration of the flow meter shall be ≤2%.

NOTE The use of an uncalibrated integral flow meter for the calibration of pump flow rates may result in large systematic errors.

4.3.8 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 that may also be suitable for pumped samplers.

4.3.9 Support

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

4.3.10 Gas chromatograph

A gas chromatograph fitted with a flame ionization, photoionization detector, mass spectrometric or other suitable detector, capable of detecting an injection of 0,5 ng benzene with a signal-to-noise ratio of at least 5 to 1.

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

4.3.11 Autosampler

The use of an autosampler is recommended because of the better repeatability of the injected volume of carbon disulphide.

NOTE. Autosamplers with liquid-chilled sample trays, suitable for the analysis of volatile solvents, are commercially available.

4.4 Setting of sampling flow rate

Switch on the sampling device; allow sufficient time for the flow rate to stabilize. Adjust the flow rate of the sampling device with a representative sorbent tube assembly in line, using an appropriate calibration device (4.3.7) to a value between 500 ml/min and 1000 ml/min. One end of the calibration device should be at atmospheric pressure to ensure proper operation.

Determine the flow rate by taking the average of a minimum of 3 consecutive measurements. The uncertainty in the measured flow shall be ≤ 2,5%.

4.5 Sampling

Break open both ends of the sample tube, ensuring that each opening is at least one half the inside diameter of the tube. Insert the tube into its protective holder, if any. Fit the precipitation shield, and mount the sampler in a vertical position at the appropriate site using the support (4.3.9).