SLOVENSKI STANDARD
SIST EN 14662-5:2005

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Kakovost zunanjega zraka ï Standardna metoda za doloļ anje koncentracije benzena ï 5. del: Difuzijsko vzorļ enje in doloļ anje s plinsko kromatografijo po desorpciji v topilu

Ambient air quality - Standard method for measurement of benzene concentrations - Part 5: Diffusive sampling followed by solvent desorption and gas chromatography

Außenluftbeschaffenheit - Standardverfahren zur Bestimmung von Benzolkonzentrationen - Teil 5: Diffusionsprobenahme mit anschließender Lösemitteldesorption und Gaschromatographie

Qualité de l'air ambiant - Méthode normalisée pour le mesurage de la concentration en benzene - Partie 5 : Prélevement par diffusion suivi d'une désorption au solvant et d'une analyse par chromatographie en phase gazeuse

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13.040.20	Kakovost okoljskega zraka	Ambient atmospheres

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Ambient air quality - Standard method for measurement of benzene concentrations - Part 5: Diffusive sampling followed by solvent desorption and gas chromatography

Qualité de l'air ambiant - Méthode pour le mesurage des concentrations en benzène - Partie 5 : Echantillonnage par diffusion suivi d'une désorption au solvant et d'une chromatographie en phase gazeuse

Luftbeschaffenheit - Standardverfahren zur Bestimmung von Benzolkonzentrationen - Teil 5: Diffusionsprobenahme mit anschließender Lösemitteldesorption und Gaschromatographie

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Contents

Page

Foreword

This European Standard (EN 14662-5:2005) 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of an identical text or by endorsement, at the latest by November 2005, and conflicting national standards shall be withdrawn at the latest by November 2005.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.

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, 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 typically collected over a period of several days or several weeks. A number of devices are recommended for the sampling of benzene, each device having a different range of applicability, particularly with regard to the optimum period of exposure.

The upper limit of the useful range is set by the sorptive capacity of the activated charcoal and, subject to dilution of the analysed solution, 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 sampling devices or in the 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 13005:1999, *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*

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

EN ISO/IEC 17025:2000, *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 terms and definitions apply.

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

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

rate at which the diffusive sampler collects a particular gas or vapour from the atmosphere, expressed in picograms per parts per billion[1] per minute (pg/ppb/min) or cubic centimetres per minute (cm^3/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.

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

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[1] ppb is volume fraction, $(\phi)=10^{-9}$; ppm is volume fraction, $(\phi)=10^{-6}$.

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
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]

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].

Attention is drawn to the fact that the terms Ambient Air and Limit Value are defined in Directive 96/62/EC [1].

4 Method description

4.1 Principle

The diffusive sampler is exposed to air for a measured time period. The rate of sampling is determined by prior calibration in a standard atmosphere (4.2.6) The benzene vapour migrates into the sampler by diffusion and is collected on the sorbent, normally activated carbon. The collected vapour is desorbed by a solvent, normally carbon disulphide, and the solution is analysed with a gas chromatograph equipped with a flame ionisation detector, mass spectrometer or other selective detector. The analysis is calibrated by means of vapour spiking onto a diffusive sampler or from calibration solutions of known amounts of benzene in carbon disulphide.

Information on possible saturation of the sorbent, 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 Annexes B and C. 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 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 to prepare standard solutions (4.2.7) and for the determination of the desorption efficiency (4.2.9). 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 co-eluting with benzene.

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 (4.2.7.1) or the desorption of samples (4.5.2) 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).

The internal standard may also be added to each sample, after the solvent, in order to correct for variations in the carbon disulphide volume, due to desorption heat.

4.2.4 Activated charcoal

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

4.2.5 Calibration standards

Calibration standards are preferably prepared by exposing the diffusive devices (of the same batch as those used for sampling) in a standard atmosphere of benzene (4.2.6) for an appropriate time, as this procedure most closely resembles the practical sampling situation.

The concentrations of the desorbed solutions of the devices used for sampling may then be compared directly with the solutions resulting from desorption of these calibration standards, i.e., without the need for applying corrections for desorption efficiency (4.5.5), but allowing for any difference between the exposure times of the calibration standards and samples.

If it is not practicable to prepare calibration standards in this way, then calibration solutions in carbon disulphide can be prepared (4.2.7) in order to compare the concentrations of desorbed solutions (4.5.2) with those calibration standards in the gas chromatographic analysis.

4.2.6 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 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 Preparation of calibration solutions in carbon disulphide

4.2.7.1 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 [12]. In general, procedures based on gravimetry and volumetry may be used to prepare calibration solutions under the conditions described below.

4.2.7.2 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 (4.2.9) 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.

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) shall be less than ± 0,1 mg.

4.2.7.3 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 (4.2.7.2) may be used to prepare calibration standard solutions in the appropriate benzene concentration range, using calibrated flasks, vials, syringes and pipettes.

4.2.8 Stability of calibration solutions

Storage times for calibration solutions vary according to application. In the above examples, calibration solutions described in 4.2.7.2 or 4.2.7.3 are stable for at least one year when stored in dark glass bottles with suitable caps at below 4 °C.

Typically, solutions described in 4.2.7.2 or 4.2.7.3 should be prepared fresh monthly, or more frequently if evidence is noted of deterioration.

4.2.9 Standards for desorption efficiency

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.

This is the procedure usually recommended by manufacturers: follow the manufacturer's guidance for specific instructions. These will vary significantly with the sampler type, and some examples are given in Annexes A, B and C. In principle, load the devices by injecting aliquots of standard solutions (4.2.7.2 or 4.2.7.3) of accurately known mass or volume at three or more levels onto clean samplers, seal the samplers and leave to equilibrate.

4.3 Apparatus

The following specific items of laboratory apparatus are required.

4.3.1 Diffusive samplers

A number of solvent-desorption diffusive samplers are available commercially. Information on available devices is given in Annex A. Data on the characteristics of two typical sampler types are given in Annexes B and C.

If required, the desorption efficiency (*D*) for each batch of samplers shall be checked by one of the methods described (4.5.5). If *D* is lower than 0,9 (90 %), the diffusive samplers shall not be used.

4.3.2 Syringes

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

4.3.3 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.

4.3.4 Support

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

4.3.5 Gas chromatograph

A gas chromatograph fitted with a flame ionization (FID), photo-ionization (PID), 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.

4.3.6 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 Sampling

Select a diffusive sampler appropriate for the compound or mixture to be sampled. Guidance on the availability of suitable samplers is given in Annex A. Annexes B and C give information on the diffusive uptake rates for two typical devices.

Mount the sampler at the appropriate site, using the support (4.3.4), and fit the precipitation shield (4.3.3). Follow the manufacturer's guidance for specific sampling instructions for the actual period of sampling. These will vary significantly with the sampler type, and some examples are given in Annexes B and C. In principle, any protective cover is removed before the diffusive sampler is exposed to the target atmosphere, and the sampler is re-sealed again at the end.

For sampling ambient air recommendations for site selection and for the protection of samples from adverse environmental conditions are given in EN 13528-3. Attention has to be paid to three main considerations: air velocity, protection from precipitation, and security.

Expose the sampling tubes only under conditions where the face velocity requirement can be expected to be satisfied.

The recommended exposure time for the devices covered by this part of EN 14662 depends on the sampler design. Different designs of diffusive sampler have different diffusive sampling rates and the exposure time will have to be selected to bring the collected mass of benzene into the calibration range of the calibration solutions (4.2.7.2 or 4.2.7.3). For example, a type A sampler exposed to an atmosphere of 5 μg/m^3 benzene for 4 weeks and desorbed in 2,0 ml carbon disulphide will result in a solution (assuming 100% desorption efficiency) of approximately 0,9 μg/ml, whilst a type B sampler exposed for 4 days and desorbed in 2 ml carbon disulphide will result in a solution of approximately 1,3 μg/ml. Sampling over longer or shorter periods is possible, provided that the resulting solution is within the concentration range of the calibration standards (0,5 μg/ml to 50 μg/ml) and any dependency of the diffusive sampling rate on the concentration and/or sampling time has been established.

Samplers should be uniquely labelled. Solvent-containing paints and markers or adhesive labels should not be used to label the samplers.

Knowledge of the average temperature and barometric pressure of the sampled air is required in order to express concentrations reduced to standard conditions (4.6). This information may be obtained from measurements on the site using a traceably calibrated thermometer and barometer. Alternatively information from a nearby weather station may be used.

Field blanks should be prepared by using tubes identical to those used for sampling and subjecting them to the same handling procedure as the samples except for the actual period of sampling. Label these as blanks.