



BSI Standards Publication

Ambient air quality — Standard method for measurement of benzene concentrations

Part 1: Pumped sampling followed by thermal desorption and gas chromatography

National foreword

This British Standard is the UK implementation of EN 14662-1:2023. It supersedes BS EN 14662-1:2005, which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee EH/2/3, Ambient atmospheres.

A list of organizations represented on this committee can be obtained on request to its committee manager.

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mesurage de la concentration en benzène - Partie 1 :
Prélèvement par pompage suivi d'une désorption
thermique et d'une chromatographie en phase gazeuse

Außenluft - Verfahren zur Messung von
Benzolkonzentrationen - Teil 1: Probenahme mit einer
Pumpe, gefolgt von Thermodesorption und
Gaschromatographie

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European foreword

This document (EN 14662-1:2023) 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of an identical text or by endorsement, at the latest by June 2024, and conflicting national standards shall be withdrawn at the latest by June 2024.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 14662-1:2005.

In comparison with the previous edition, the following technical modifications have been made:

- inclusion of the option of multi-tube sampling devices such that a series of samples can be collected sequentially and/or in parallel without user intervention in the field;
- specification of associated ‘type testing’ requirements to allow multi-tube sampling devices to be tested and approved;
- inclusion of gas standard calibration options, alongside liquid spiking, in line with best practice;
- extensive updates to technical aspects, including uncertainty calculations, in line with the latest standards.

Any feedback and questions on this document should be directed to the users’ national standards body. A complete listing of these bodies can be found on the CEN website.

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

1 Scope

This document gives general guidance for the sampling and analysis of benzene in air by pumped sampling, thermal desorption and capillary gas chromatography.

This document is in accordance with the generic methodology selected as the basis of the European Union reference method 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 document is valid for the measurement of benzene in a concentration range of approximately $0,5 \mu\text{g}/\text{m}^3$ to $50 \mu\text{g}/\text{m}^3$. Air samples are typically collected over periods ranging from a few hours to 7 days.

The upper limit of the useful range is set by the sorptive capacity (the safe sampling volume) of the sorbent and by the linear dynamic range of the gas chromatograph column and detector or by the sample splitting capacity 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 graphitised carbon sorbents, but higher levels of aromatic hydrocarbons have been noted in other sorbents – e.g. porous polymers. The detection limit will be approximately 1/10 of the lower concentration range.

This document provides general guidance for the sampling of benzene using either a single sampling device, which is changed manually after every exposure period, or sequential sampling device capable of storing and exposing multiple samples without user intervention. The analysis methods are diverse, but a suitable approach for analysing samples and blanks and calculating benzene levels is described in Annex B.

NOTE The method described in this document can be used for the determination of other compounds besides benzene, under the condition of documented validation tests.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

EN ISO 16017-1, *Indoor, ambient and workplace air - Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography - Part 1: Pumped sampling (ISO 16017-1)*

3 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at <https://www.electropedia.org/>
- ISO Online browsing platform: available at <https://www.iso.org/obp>

3.1

breakthrough volume

volume of a vapour-in-air sample for a sorbent tube/analyte combination that can be passed through the front section of a sorbent tube before the eluting concentration of the analyte vapour reaches 5 % of the applied test concentration

3.2

calibration gas mixture

traceable gas mixture of sufficient stability and homogeneity whose composition is properly established for use in the calibration of a measuring instrument or for the validation of a measurement or gas analytical method

3.3

certified reference material

CRM

reference material (RM) characterized by a metrologically valid procedure for one or more specified properties, accompanied by an RM certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability

[SOURCE: ISO Guide 30:2015, 2.1.2 [2]]

3.4

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

[SOURCE: JCGM 100:2008, 2.3.4 [3]]

3.5

competent authority

organization which implements the requirements of EU Directives and regulates installations, which complies with the requirements of applicable European Standards

Note 1 to entry: In ambient air quality monitoring this is an authority that performs one or more of the tasks listed in Article 3 of Directive 2008/50/EC.

3.6

competent body

organization which can demonstrate its competence for a specific task to the competent authority in the Member State

Note 1 to entry: It is recommended that the competent body performing the required tests be able to demonstrate that it works in conformity with the requirements of internationally accepted standards for test laboratories.

Note 2 to entry: EN ISO/IEC 17025 is the harmonized internationally accepted standard that applies.

Note 3 to entry: A formal accreditation by a member body of the European Accreditation Organization to EN ISO/IEC 17025 is a demonstration of conformity.

3.7

desorption efficiency

ratio of the mass of analyte desorbed from a sampler to that collected

3.8**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

Note 1 to entry: The fraction may be viewed as the coverage probability or level of confidence of the interval.

Note 2 to entry: To associate a specific level of confidence with the interval specified by the expanded uncertainty requires explicit or implicit assumptions regarding the probability distribution characterized by the measurement result and its combined standard uncertainty (3.4). 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.

[SOURCE: JCGM 100:2008, 2.3.5] [3]

3.9**reference material****RM**

material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process

[SOURCE: ISO Guide 30:2015, 2.1.1] [2]

3.10**repeatability condition of measurement****repeatability condition**

condition of measurement, out of a set of conditions that includes the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time

[SOURCE: JCGM 200:2012, 2.20] [4]

3.11**retention volume**

elution volume at peak maximum of a small aliquot of a benzene vapour eluted from the tube by air or chromatographic carrier gas

3.12**safe sampling volume****SSV**

volume of air that can be safely drawn through a sampler under prescribed conditions without significant breakthrough of benzene

Note 1 to entry: See EN ISO 16017-1 for more information.

3.13**sample delivery**

inert assembly of components needed to transfer the air to the sampling device (3.15) or sequential sampling device (3.17) inlet without impacting the concentration of benzene

3.14**sampler**

sampling tube packed with a known mass of sorbent to retain benzene from ambient air

3.15

sampling device

device capable of exposing one or more samplers (3.14) to a constant flow of air for one prescribed sampling period, until the required volume of air has been sampled

3.16

sampling efficiency

ratio of the mass of analyte collected by a sampler (3.14) to that applied

3.17

sequential sampling device

automated sampling device capable of storing multiple samplers (3.14) and exposing them in sequence to a constant flow of air for prescribed periods without user intervention, until all the required volumes of air have been collected in the samplers

3.18

signal to noise ratio

measure that compares the level of the signal to the level of background noise

Note 1 to entry: It is also possible to estimate the chromatographic detection limit with the aid of the signal-to-noise ratio. For example, the mean noise level can be estimated across a distance of ten half-peak widths before and after the peak. The threefold of this noise level is then defined as the detection limit [5].

3.19

standard uncertainty

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

[SOURCE: JCGM 100:2008, 2.3.1] [3]

3.20

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 to entry: 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 to entry: 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 characterized by experimental standard deviations. The other components, which can also be characterized by standard deviations, are evaluated from assumed probability distributions based on experience or other information.

Note 3 to entry: 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

[SOURCE: JCGM 100:2008, 2.2.3] [3].

Attention is drawn to the fact that the terms Ambient Air and Limit Value are specified in Directive 2008/50/EC [1].

4 Method description

4.1 Principle

A measured volume of sample air is drawn through a sampler (3.14). Provided suitable sorbents are chosen, benzene is retained by the sorbent and thus is removed from the flowing air stream. The collected vapour (on each sampler) is desorbed by heat and is transferred under inert carrier gas into a gas chromatograph equipped with a chromatography column and a suitable detector, where it is analysed. The equipment shall be calibrated by one of the following means:

- Vapour or liquid spiking onto a sampler;
- Reference material (3.9) in sampler.

4.2 Reagents and materials

The determination of the impurities contained in each material (gas or liquid) used in the preparation has an impact on the uncertainty (3.20) associated with the content of the component. Requirements for the purity analysis of reagent and materials used in the preparation of calibration standards for gases are described in ISO 19229:2019 [7].

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

4.2.1 Benzene

Benzene is required for calibration purposes, using either vapour spiking (4.2.6 to 4.2.7) or liquid spiking (4.2.8 to 4.2.10) onto samplers (3.14). The benzene used shall be of a minimum purity of 99,5 %.

4.2.2 Dilution solvent

A dilution solvent is required for preparing calibration blend solution for liquid spiking (4.2.8). The presence of benzene impurity in the solvent or any other gas chromatographic interferent with benzene shall be assessed and it shall be lower than 10 % of the lowest mass of benzene introduced as a calibration standard. During the assessment of the purity the same volume shall be introduced as the volume of the lowest calibration standard.

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 Dilution gas

Dilution gas, such as dry air or nitrogen, is required for preparing calibration gas mixtures (3.2), for preparation of calibration standards in samplers (3.14) and for sampler cleaning. The presence of benzene impurity in the gas or any other gas chromatographic interferent with benzene shall be lower than 10 % of the lowest mass of benzene introduced as a calibration standard. During the assessment of the purity the same volume shall be introduced as the volume of the lowest calibration standard.

4.2.4 Inert gas for sampler conditioning

The purity of the inert gases used for sampler (3.14) conditioning, typically nitrogen or helium, shall be such that the conditioned samplers meet the blank requirements specified in Table 1.

Oxygen filters are recommended in the inert gas supply line to minimize the risk of sorbent oxidation.

4.2.5 Calibration standards in samplers

Calibration standards in samplers (3.14) are preferably prepared by loading the required amount of benzene in vapour phase on the samplers from calibration gas mixtures (3.2) (see 4.2.6 and 4.2.7) as this procedure most closely resembles the practical sampling situation.

NOTE 1 The loading ranges given in 4.2.7 to 4.2.10 are not mandatory and approximate to the application range given in the scope.

If this way of preparation is not practicable, calibration standards may be prepared by a benzene liquid spiking procedure (see 4.2.8 to 4.2.10) 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, or,
- b) confirmed by comparison with reference materials (3.9) (if available), standards produced using calibration gas mixtures, or results of reference measurement procedures.

NOTE 2 See 4.2.10 relating to the mass of solvent retained in the calibration standard.

To minimize matrix effects, calibration standards should be closely matched to the samplers with respect to sorbent type, particle size and mass of sorbent.

Calibration standards are required at a minimum of 5 mass levels for a full calibration (4.7.3) and the mass range of benzene shall cover the maximum range of benzene masses that are expected to be collected/trapped during field monitoring.

Maximum permitted uncertainty (3.20) in the preparation of calibration standards in samplers is 5 % with a level of confidence of 95 %.

4.2.6 Preparation of calibration gas mixtures

Prepare calibration gas mixtures (3.2) of known concentrations of benzene by a recognized procedure. Methods described in EN ISO 6142-1 [8], EN ISO 6144 [9] and EN ISO 6145-1 [10] are suitable. If the procedure is not applied under conditions that will allow the establishment of full metrological traceability of the generated concentrations to primary standards of amount of substance, mass and/or volume, the concentrations need to be confirmed using an independent procedure, e.g. EN ISO 6143 [11] or ISO 12963 [12].

For the conversion of the calibration gas mixture composition into mass concentration (mass per volume) use e.g. EN ISO 14912 [13].

NOTE Calibration gas mixtures can be prepared or obtained at the full range of benzene ambient concentration levels. The lower concentrations ($0,5 \mu\text{g}/\text{m}^3$ to $5 \mu\text{g}/\text{m}^3$) are typically obtained by dynamic methods (ISO 6145-1).

4.2.7 Calibration standards in samplers prepared by vapour spiking of calibration gas mixtures

Prepare loaded samplers (3.14) by passing an accurately known volume of the calibration gas mixture (3.2) through the sampling end of conditioned samplers e.g. by means of a constant controlled flow using a pump as described in 4.5 and 4.6. The volume of calibration gas sampled shall not exceed the safe sampling volume (3.12) of the sorbent. After loading the sampler 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 ensure consistency of detector response.

NOTE In ambient air monitoring, benzene masses collected typically range from 5 ng to 5 μg per sampler. Therefore, loading volumes of 1 l of a $5 \mu\text{g}/\text{m}^3$ calibration standard to 10 l of a $500 \mu\text{g}/\text{m}^3$ calibration standard, will allow covering the lower and upper concentration ranges.

4.2.8 Preparation of standard solutions for liquid spiking

4.2.8.1 General

The recommended approach for preparation of standard solutions is by gravimetry.

4.2.8.2 Solution containing approximately 5 mg/ml of benzene

Weigh a 100 ml volumetric flask and introduce approximately 75 ml of dilution solvent (4.2.2) into a 100 ml volumetric flask. Then weigh approximately 500 mg benzene into the flask. Make up to 100 ml with dilution solvent, stopper, weigh and shake to mix.

In order to ensure an uncertainty (3.20) of the mass of benzene introduced appropriate to the application the weighing uncertainty of the equipment used ($k = 2$) shall be less than $\pm 70 \mu\text{g}$.

Dilute this stock solution down to appropriate concentrations to provide masses that match those expected during ambient air monitoring.

NOTE In ambient air monitoring, benzene masses collected typically range from 5 ng to 5 μg per sampler (3.14). Therefore, loading 1 μl volumes of liquid standard solutions within the concentration range 5 $\mu\text{g}/\text{ml}$ to 5 mg/ml will allow covering the lower and upper concentration ranges.

4.2.9 Stability of standard solutions

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

4.2.10 Calibration standards in samplers prepared by liquid spiking of standard solutions

Prepare calibration standards by introducing 1 μl of a liquid standard solution into the sampling end of conditioned samplers (3.14) in a stream of dilution gas using a calibrated precision 1 μl syringe. A sampler is fitted to a suitable ambient temperature injection facility, incorporating a septum inlet, through which dilution gas is introduced at 100 ml/min. Inject the standard solution through the septum and purge for at least 5 min. The sampler is then disconnected and sealed. Prepare fresh calibration standards with each batch of samples. The samplers used for calibration shall be kept at ambient temperature.

Depending on the dilution solvent volatility and associated choice of sampler sorbent it may or may not be possible to selectively purge the dilution solvent during the loading process without compromising retention of benzene. Liquid standard injection volumes should be kept to 1 μl or below to minimize solvent interference in the subsequent analysis because in most cases it is not possible to selectively purge the solvent.

NOTE Use PTFE or similar fittings to connect the sampler to the injection facility such that they ensure a leak tight seal without damaging the end of the sampler.

4.3 Apparatus

The following specific items of laboratory equipment are required.

4.3.1 Samplers

These samplers (3.14) shall be compatible with the thermal desorption apparatus to be used (4.3.8). Typically, but not exclusively, they are constructed of stainless steel tubing, 6,4 mm (1/4 inch) OD, 5 mm ID and 90 mm long. Samplers of other dimensions may be used but the safe sampling volumes (SSV) (3.12) given in Annex A are based on these sampler dimensions. One end of the sampler is marked, for example by a scored ring about 10 mm from the sampling inlet end. The samplers are packed with preconditioned sorbent so that the sorbent bed will be within the desorber heated zone and a gap of at least 14 mm is retained at each end to minimize errors due to diffusive ingress at very low pump flow

rates. Samplers contain between 200 mg and 1000 mg sorbent, depending on sorbent density. The sorbents are retained by stainless steel gauzes and/or unsilanised glass wool plugs.

4.3.2 Sampler and caps

The samplers (3.14) shall be sealed, according to the requirements of EN ISO 16017-1 or equivalent, e.g. with metal screw cap fittings with PTFE seals.

4.3.3 Types of sampling devices

4.3.3.1 General

There are a number of possible configurations for sampling devices (3.15), which would meet different specific requirements.

For all the sampling devices described below, the flow rate and sampling time should be such that the safe sampling volumes (3.12) specified in Annex A are not exceeded.

Potential configurations for sampling devices are presented below.

4.3.3.2 Single sampling device

Sampling device (3.15), incorporating a sampler (3.14), capable of maintaining a constant calibrated flow rate of air in the range 5 ml/min to 200 ml/min throughout the required sampling period (typically a few hours to 7 days). As such, the following flow control mechanisms may be used:

- a pump with an adjustable flow rate;
- a vacuum pump with a critical orifice;
- a mass-flow controller operated by a vacuum pump;
- a vacuum pump with a constant pressure drop over a restriction.

The flow rate and sampling time should be such that the safe sampling volumes (3.12) specified in Annex A are not exceeded.

The flow rate and sampling time should allow collection of at least 20 ng of benzene on the sampler to minimize the analytical uncertainty (3.20).

NOTE If a mass flow controller is not used in the system, then measurements of temperature and pressure will be required to evaluate the sampling volume.

4.3.3.3 Multiplexing sampling device

This type of device is similar to that described in 4.3.3.2 above, except that instead of a single sampler (3.14), two or more samplers are connected in parallel and the flow of sampled air is switched through the different samplers at regular intervals to extend the overall sampling period and the time between changeover visits.

4.3.3.4 Parallel sampling device

This type of device is a variation on that described in 4.3.3.3 above, where two or more samplers (3.14) can be configured to sample simultaneously (i.e. in parallel). This may be desirable if multiple analyses are required or as a cross-check on sampling efficiency (3.16). Different sample flows for each sampler may be required. Other requirements for operation are identical to 4.3.3.2.

4.3.4 Sequential sampling devices

4.3.4.1 General

There are a number of possible configurations for sequential sampling devices (3.17), which would meet different specific requirements.

Potential configurations for sequential sampling devices are presented below.

4.3.4.2 Individual sequential sampling device

An automated device that stores multiple samplers (3.14) for collecting samples one after the other (sequentially). It shall be capable of maintaining a constant calibrated flow rate of air in the range 5 ml/min to 200 ml/min throughout the entire sampling period (typically a few hours to 7 days) for each sampler.

The first sampler is selected and a known volume of ambient air is drawn through it while all the other samplers are kept sealed. After the sampling time for that sampler is complete, it is resealed and air is drawn through the next sampler.

Each phase of the process (sampling, storage before and after sampling), will be managed by the sequential sample device to ensure that samplers are protected both from artefact ingress (e.g. cross contamination, exposure to enclosure air or ambient air) and analyte loss for the entire period they are inside the sequential sampling device (3.17). For each individual sampler, the sequential sampling device shall allow users to set and record the flow rate and duration of sampling. Other information that shall be recorded includes: date and time of sampling, variation in flow rate and total volume of air sampled at 20°C and 101,3 kPa.

The sequential sampling device shall have the capacity to accommodate field blanks as described in 4.6. The field blank shall be sealed and stored identically to the other samplers.

4.3.4.3 Parallel sequential sampling device

This type of device is a variation on that described in 4.3.4.2 above, where two or more samplers (3.14) can be configured to sample simultaneously (i.e. in parallel). This may be desirable if multiple analyses are required or as a cross-check on sampling efficiency (3.16). Different sample flows for each sampler may be required. Other requirements for operation are identical to 4.3.4.2.

4.3.4.4 Other functionality

It may also be desirable to be able to accommodate:

- Different sampler diameters / sampler lengths;
- Programmable sampler selection;
- Online access to sampling device (3.15) operation / configuration and operational parameters via RS232/Ethernet/wireless communication;
- Protocol for dealing with power interruption / sampling restart;
- Automated electronic confirmation of sampler identity;
- Ability to include backup sampler.

For all of these possible options, preserving the integrity of the samplers (3.14) before, during and after sampling is essential.

4.3.5 Tubing

All components of the sampling device (3.15) and sample delivery (3.13) shall not influence the measurement of benzene.

Tubing used to connect the outlet of the sampler (3.14) to the pump or pumping mechanism shall be of appropriate length and internal diameter to ensure a leak-proof fit to both pump and sampler or sampler holder, if used.

Tubing used to connect the sampling device to measure ambient air shall be of appropriate length and internal diameter to ensure a leak-proof fit to the inlet of the sampling device. The flow of ambient air through this external tube shall be sufficient to ensure the total loss of sample gas to the sampling system is less than 2 %.

Inert and non-outgassing materials should be used e.g. PFA, PTFE, FEP, PVDF, stainless steel (316SS), inert coated SS, borosilicate glass.

4.3.6 Flow calibration device

A flow meter that is traceably calibrated to a primary flow standard over the desired flow range (4.3.4.2). The uncertainty (3.20) in the calibration of the flow meter shall be $\leq 2\%$ for flow checks, and $\leq 1\%$ for flow calibrations.

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

4.3.7 Gas chromatograph

A gas chromatograph fitted with a suitable detector, capable of detecting 0,5 ng benzene with a signal-to-noise ratio of at least 5 to 1 and providing linearity of benzene over at least 3 orders of magnitude.

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

4.3.8 Thermal desorption (TD) apparatus

Apparatus for the two-stage thermal desorption of the samplers (3.14) 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 sampler to be desorbed whilst they are heated and purged simultaneously with inert carrier gas. Important features for reliable analytical thermal desorption operation include:

- a) sealing of samplers before and after desorption to prevent loss of analytes or ingress of laboratory air artefacts;
- b) robust leak testing of each sampler before desorption occurs. (Leak testing at ambient temperature and without flow maintains the integrity of samplers which fail the leak test such that they can be checked and analysed later);
- c) pre-purging of air from samplers before desorption to prevent analyte or sorbent degradation.

The desorption temperature and time are adjustable, as is the carrier gas flow rate. In two-stage desorption analytes swept from the sampler are refocused on a small sorbent cold trap or cryofocusing device, before rapid secondary desorption subsequently injects or transfers benzene into the capillary GC column in a narrow band of vapour thus minimizing peak widths and optimizing sensitivity. Both primary desorption (of the sampler) and secondary desorption (of any sorbent focusing trap) shall take place with carrier gas flowing in the reverse (back-flush) direction to the flow of air/gas during sampling/trapping.

NOTE 1 The apparatus can also incorporate additional features, such as automatic sampler loading, automatic addition of gas-phase internal standard onto the sampling end of samplers before desorption, automatic dry purging

of samplers with carrier gas flowing through the sampler in the sampling direction (used before desorption to minimize water interference when analysing humid air samples), the option of sample splitting during primary desorption (between the sampler and the focusing trap) and the option for quantitative re-collection of split flow for repeat analysis and method/data validation.

The desorbed sample, contained in the carrier gas, shall be delivered to the gas chromatograph and capillary column via a heated transfer line. A split option should be included at this stage to reduce the mass of benzene reaching the GC-analytical system if required.

NOTE 2 More information is given in informative Annex B.

4.4 Sampler conditioning and blank profiling

4.4.1 General

Samplers (3.14) prepacked and preconditioned by the manufacturer are available for most sorbents.

4.4.2 Initial conditioning

A particle size 0,18 mm to 0,60 mm (30 to 80 mesh) is recommended. For carbon based sorbents a minimum size of 0,25 mm is recommended. Sorbent particle sizes larger than 0,18 mm to 0,60 mm may be used but the breakthrough characteristics given in Annex A may be affected. Smaller sorbent particle size ranges are not recommended because of back pressure problems. Each sorbent should ideally 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 samplers (3.14). To prevent recontamination of the sorbents, they shall be kept in a clean atmosphere during cooling to room temperature, storage, and loading into the samplers. Freshly packed samplers shall also be stringently conditioned, at temperatures above analytical desorption conditions but below the sorbent maximum, and in a flow of 30-200 ml/min inert gas (typically nitrogen or helium) for several hours. The inert gas flow shall be in a direction opposite to that used during sampling. Wherever possible, analytical desorption temperatures should be kept below those used for conditioning. Once conditioned, all samplers shall be capped and sealed (4.3.2) and stored at room temperature in an uncontaminated environment.

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.

4.4.3 Ongoing conditioning

Prior to use, samplers (3.14) shall be re-conditioned by desorbing them at a temperature at or just above the analytical desorption temperature (see Annex D). Conditioning time will range from 10 min to several hours, depending on the sorbent, with a carrier gas flow of 30-200 ml/min. The inert gas flow shall be in a direction opposite to that used during sampling.

Samplers shall be sealed with metal screw caps with combined PTFE ferrule fittings (4.3.2) and stored in an airtight, non-emitting container, not subject to extreme temperature fluctuations, when not sampling or being conditioned.

In any case, the samplers shall be reconditioned before use if they have been stored for more than three months.

4.4.4 Testing of blanks

At least 10 % of the samplers (3.14) (minimum of 3 samplers) shall be analysed, using routine analytical parameters, to ensure that the thermal desorption blank is sufficiently small. If the blank is unacceptable, the batch of samplers shall be reconditioned under the same or more stringent conditions. If blank performance remains unacceptable, the sorbent material shall be replaced. Once a sample has been analysed, the sampler may be reused to collect a further sample immediately. However, it is advisable to re-check thermal desorption blank if the samplers are left for an extended period before reuse, or if sampling for a different analyte is envisaged. The maximum mass of benzene in the blanks shall conform to the requirement in Table 2.

4.5 Setting of sampling flow rate

Calibrate the flow of the sampling device (3.15) with a representative sampler (3.14) assembly in line, using an appropriate external calibrated meter (4.3.6).

Determine the flow rate by taking the average of a minimum of 3 consecutive measurements. The uncertainty (3.20) in the measured flow shall be $\leq 2,5$ %.

The output end of the calibrated flow meter should be at atmospheric pressure to ensure proper operation.

4.6 Sampling

Attach / insert the sampler(s) (3.14) into the sampling device (3.15) ensuring the correct orientation of the sampler(s) relative to the sample flow. Turn the device on and measure the flow rate and/or adjust the flow rate so that the required sample volume is taken in the available time (see 4.3.3.2).

Sampling efficiency (3.16) will be 100 % (quantitative), provided the safe sampling volume (3.12) of the sorbents is not exceeded. If this capacity is exceeded, breakthrough of benzene from the sampler assembly will occur. The breakthrough volume (3.1) may be measured by sampling from a standard vapour atmosphere, whilst monitoring the effluent air with a flame ionization or equivalent detector (a suitable method is described in Annex C). Alternatively, for relatively hydrophobic sorbents, instead of determining the breakthrough volume directly, the mathematically related retention volume may be determined. The retention volume is determined chromatographically at elevated temperatures and subsequent extrapolation to room temperature. A suitable method is described in Annex D.

The safe sampling volumes of sorbents will vary with ambient air temperature, (e.g. for porous polymers, reducing by a factor of about 2 for each 10 °C rise in temperature). To allow a suitable margin of safety, a safe sampling volume (SSV) is specified such that it is a volume of not more than 70 % of the 5 %-breakthrough volume (see C.1.1) or 50 % of the retention volume (see C.1). Annex A gives typical values for retention volumes and safe sampling volumes. These values have been determined by the chromatographic method (Annex D).

NOTE The safe sampling volumes in Annex A have been determined by the chromatographic method (Annex D) Measurements by the direct method (Annex C) [14] indicate that the chromatographic method is a reliable indication of the true breakthrough capacity except under conditions of high concentrations or very high humidity. These measurements [14] indicate that breakthrough volumes at high (80 %) humidity are about a factor of two lower for porous polymers, and the effect could be significantly greater for some types of carbon sorbents.

If the sample is important and the chance of overload and/or sample breakthrough is a possibility, a second sample at a lower flow rate should be taken.

Record the sampling period for each sample taken. Measure the flow rate again at the end of the period of unattended operation as described in 4.5. Sample flow shall meet the requirement 5 in Table 1. Where continuous flow measurement is not possible, the sample flow at the beginning and end of the sampling period shall be recorded.

For sampling devices that use a volumetric flow measurement, knowledge of the average temperature and barometric pressure of the sampled air is required in order to express concentrations reduced to standard conditions. This information may be obtained from measurements on the site using a traceably calibrated thermometer and barometer. For further information, see EN ISO 16017-1.

At the end of the sampling period (single sampler or series of samplers) the sampler assembly shall be disconnected and both ends of each sampler shall be sealed with compression seals (4.3.2). Tighten these seals securely, but without deforming the ends of the sampler. The samplers should be uniquely labelled. Solvent containing paints and markers or adhesive labels should not be used to label the samplers.

Sealed samples shall be stored in such a way that contamination cannot occur as described in 4.4.

Field blanks should be prepared by using samplers identical to those used for sampling and subjecting them to the same handling procedure as the samplers except for the actual period of sampling. Label these as blanks. For sequential sampling devices (3.17), at least one field blank shall be installed, but no flow shall be drawn through it during the entire exposure period. An additional, fully capped blank shall be kept next to the sampling device as an additional comparison. Results from these blanks shall meet the criteria given in Table 1 in 6.2.

The analysis methods are diverse, but a suitable approach for analysing samples and blanks and calculating benzene levels is described in Annex B.

5 Air inlet/manifold sampling equipment

5.1 General

Depending on the system, a dedicated sampling line may be chosen. Alternatively, sampling can take place from a common sampling inlet to which other systems and equipment may be attached. Conditions and layout of the sample delivery (3.13) will contribute to the uncertainty of the measurement (3.20); to minimize this contribution to the expanded uncertainty (3.8), requirements for the sampling equipment are given in the following subclauses.

NOTE In Annex H, different arrangements of the sampling equipment are schematically presented.

5.2 Sampling location

5.2.1 General

Guidance and criteria on sampling points on a micro scale are given in Annex III of Directive 2008/50/EC [1] and the amendment (EU) 2015/1480 [15].

5.2.2 Protective shield

The ambient air inlet shall be equipped with a protective shield to prevent contamination, e.g. particles, water droplets, insects, etc. The sampling end is normally oriented downwards.

NOTE EN 13528-3 [16] describes various shields for diffusive samplers that can also be suitable for pumped samplers.

5.2.3 Positioning of the inlet

In the event of a sampling device (3.15) being used in an outdoor standalone cabinet, it shall be equipped with a device capable of positioning the sampling device and sampler (3.14) at the appropriate height and distance from obstacles to warrant undisturbed sampling.

5.3 Sample delivery

5.3.1 General

Sample delivery (3.13) describes the mechanism by which ambient air is delivered to the sampler (3.14). This can range from a simple sampler, suitably protected to prevent water and dust ingress to the sampler, through to a multi pollutant sampling manifold system, to which the sampler is connected by means of additional tubing.

The sampling device (3.15) itself may contain tubing and mechanisms to deliver this air to the sampler, but this is considered separately to the sample delivery.

5.3.2 Construction

The sample delivery (3.13) shall include a sampling inlet and may include the following components:

- a sampling line or manifold;
- a particle filter placed between the sampling line or manifold and the sampler (3.14);
- an additional pump where a sampling manifold is used.

The sample inlet shall be constructed to prevent condensation and to ensure that ingress of rainwater into the sampling line or manifold is prevented. The sampling line or manifold shall be as short as practical and the air flow through it shall be sufficient to minimize the residence time. The material of the sample inlet as well as the sampling line or manifold can influence the composition of the sample. These shall be chemically inert to benzene. The influence on the measured concentrations as a result of the residence time inside the sampling inlet shall be $\leq 2,0 \%$ (see Annex D [EN 14662-3] [17]).

5.3.3 Particle filter

A particle filter may be used to protect the sorbent in the sampler (3.14) from contamination. An additional particle filter may also be used to protect the sample flow control apparatus from particle deposition. The influence of the particle filter on the measured concentrations of benzene shall be $\leq 2,0 \%$.

If a particle filter is used to protect the sorbent sampler, the material of the filter and its housing shall be chemically inert to benzene. The particle filter shall be accessible for inspection and periodic replacement.

NOTE 1 A pore size of the filter of $5 \mu\text{m}$ usually fulfils this requirement.

NOTE 2 Suitable materials for the filter housing are, for example, PTFE, stainless steel, or borosilicate glass.

The filter shall be changed periodically depending on the dust loading at the sampling site (as indicated in 9.7). The filter housing shall be cleaned or replaced at least every year.

NOTE 3 Overloading of the filter can cause loss of benzene by adsorption on the particle matter and can increase the pressure drop in the sampling line.

5.3.4 Conditioning

The sample delivery (3.13) and the particle filter shall be conditioned after initial installation and/or replacement for a period of at least 30 min at the maximum air sampler flow rate.

NOTE Conditioning during field operation is considered a part of normal maintenance. Manifold pump or fan

When a sampling manifold is used, an additional pump or fan is necessary for moving ambient air through the sampling manifold, see 5.3. The inlet of the sampling pump or fan for the sampling manifold shall be

located at the end of the sampling manifold. The sampling pump or fan shall have sufficient rating to ensure that all systems connected to the manifold are supplied with the required amount of air. To verify functioning of this pump or fan, it is recommended to install a flow alarm system. An example of a sampling manifold is given in Annex H.

6 Type testing

6.1 General

The type testing of a sampling device (3.15) according to Clause 6 and subsequent QA/QC and verification procedures according to Clause 7 provide evidence that the specified requirements concerning data quality objectives laid out in relevant EU Directives can be satisfied. A competent body (3.6) shall perform the type testing. The type testing shall be awarded by, or on behalf of, the competent authority (3.5) of a member state.

The type testing is based on the evaluation of performance characteristics determined under a prescribed series of tests. In this European Standard, test procedures are described for the determination of the actual values of the performance characteristics for at least two identical sampling devices in a laboratory and two sampling devices in the field. The evaluation for type testing of a sampling device establishes the contribution to the expanded uncertainty (3.8) of the sampling device to the measurement.

For the purposes of type testing, one sorbent material shall be used.

The sampling procedure shall not increase the expanded uncertainty (3.20) beyond the level specified by Annex I of Directive 2008/50/EC [1].

6.2 Relevant performance characteristics and performance criteria

The performance characteristics which shall be determined during a laboratory and field test, and their related performance criteria, are given in Table 1. Table 1 applies to those ranges that are specified as normative in the scope of this European Standard.

The determination of the value of the performance characteristics stated in Table 1 shall be performed by a competent body (3.6) during the laboratory test and field test according to the procedures described in 6.3 and Annex E.