BS EN 14662-3:2015

BSI Standards Publication

Ambient air — Standard method for the measurement of benzene concentrations

Part 3: Automated pumped sampling with in situ gas chromatography

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National foreword

This British Standard is the UK implementation of EN 14662-3:2015. It supersedes BS EN 14662-3:2005 which is withdrawn.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 secretary.

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Ambient air - Standard method for the measurement of benzene concentrations - Part 3: Automated pumped sampling with in situ gas chromatography

Qualité de l'air ambiant - Méthode normalisée pour le mesurage de la concentration en benzène - Partie 3: Prélèvement par pompage automatique avec analyse chromatographique en phase gazeuse sur site

Außenluft - Messverfahren zur Bestimmung von Benzolkonzentrationen - Teil 3: Automatische Probenahme mit einer Pumpe und gaschromatographische In-situ-Bestimmung

This European Standard was approved by CEN on 17 July 2015.

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

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Contents

European foreword

This document (EN 14662-3:2015) 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of an identical text or by endorsement, at the latest by May 2016, and conflicting national standards shall be withdrawn at the latest by May 2016.

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

This document supersedes EN 14662-3:2005.

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 the Council Directive 2008/50/EC [1].

Details of significant technical changes between this European Standard and the previous edition are:

- Clause 8 has been brought in line with other Standards dealing with type approval of gas analysers;
- In 9.4 and 9.6, performance requirements have been modified or removed and additional performance criteria and tests have been introduced for repeatability at span level;
- In 9.5, formulae have been introduced for software adjustment of the raw analyser signal after calibration;
- In Annexes E and F, uncertainty calculations have been modified to be in conformity with EN ISO 14956.

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

1 Scope

This European Standard specifies a semi-continuous measurement method for the determination of the concentration of benzene present in ambient air based on automated sampling and analysis by gas chromatography. This European Standard describes the performance characteristics and sets the relevant minimum criteria required to select an appropriate automated gas chromatograph (GC) by means of type approval tests. It also includes the evaluation of the suitability of an analyser for use in a specific fixed site so as to meet the data quality requirements as specified in Annex I of Directive 2008/50/EC [1] and requirements during sampling, calibration and quality assurance for use.

The method is applicable to the determination of the mass concentration of benzene present in ambient air in the range up to 50 µg/m^3 benzene. This concentration range represents the certification range for the type approval test.

Other ranges may be used depending on the levels present in ambient air.

NOTE 1 When the standard is used for other purposes than for measurements required by Directive 2008/50/EC, the ranges and uncertainty requirements may not apply.

The method covers the determination of ambient air concentrations of benzene in zones classified as rural areas, urban-background areas and traffic-orientated locations and locations influenced by industrial sources.

The results are expressed in µg/m^3 (at 20 °C and 101,3 kPa).

NOTE 2 50 µg/m^3 of benzene corresponds to 15,4 nmol/mol of benzene.

This European Standard contains information for different groups of users.

Clauses 5 to 7 and Annexes C and D contain general information about the principles of benzene measurement by automated gas chromatography and sampling equipment.

Clause 8 and Annex E are specifically directed towards test houses and laboratories that perform type-approval testing of benzene analysers. These sections contain information about:

- type-approval test conditions, test procedures and test requirements;
- analyser performance requirements;
- evaluation of the type-approval test results;
- evaluation of the uncertainty of the measurement results of the benzene analyser based on the type-approval test results.

Clauses 9 to 11 and Annex F are directed towards monitoring networks performing the practical measurements of benzene in ambient air. These sections contain information about:

- initial installation of the analyser in the monitoring network and acceptance testing;
- ongoing quality assurance/quality control;
- calculation and reporting of measurement results;
- evaluation of the uncertainty of measurement results under practical monitoring conditions.

2 Normative references

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

EN 15267-1, *Air quality — Certification of automated measuring systems — Part 1: General principles*

EN 15267-2, *Air quality — Certification of automated measuring systems — Part 2: Initial assessment of the AMS manufacturer's quality management system and post certification surveillance for the manufacturing process*

EN ISO 6142, *Gas analysis — Preparation of calibration gas mixtures — Gravimetric method (ISO 6142)*

EN ISO 6143, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures (ISO 6143)*

EN ISO 6144, *Gas analysis — Preparation of calibration gas mixtures — Static volumetric method (ISO 6144)*

EN ISO 6145-4, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 4: Continuous syringe injection method (ISO 6145-4)*

EN ISO 6145-6, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 6: Critical orifices (ISO 6145-6)*

EN ISO 6145-7, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 7: Thermal mass-flow controllers (ISO 6145-7)*

EN ISO 6145-8, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 8: Diffusion method (ISO 6145-8)*

EN ISO 6145-9, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 9: Saturation method (ISO 6145-9)*

EN ISO 6145-10, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 10: Permeation method (ISO 6145-10)*

EN ISO 14956, *Air quality — Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty (ISO 14956)*

ISO/IEC Guide 98-3:2008, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

3 Terms and definitions

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

3.1
adjustment

set of operations carried out on a measuring system so that it provides prescribed indications corresponding to given values of a quantity to be measured

Note 1 to entry: Types of adjustment of a measuring system include zero adjustment of a measuring system, offset adjustment, and span adjustment (sometimes called gain adjustment).

Note 2 to entry: Adjustment of a measuring system should not be confused with calibration, which is a prerequisite for adjustment.

Note 3 to entry: In the context of this European Standard, adjustment is performed on measurement data rather than on the analyser.

[SOURCE: JCGM 200:2012 (VIM), Note 3 to entry has been modified, [2]]

3.2
ambient air

outdoor air in the troposphere, excluding workplaces as defined by Directive 89/654/EEC where provisions concerning health and safety at work apply and to which members of the public do not have regular access

[SOURCE: 2008/50/EC [1]]

3.3
analyser

analytical instrument that provides an output signal which is a function of the concentration, partial pressure, flow or temperature of one or more components of a gas mixture

3.4
availability of the analyser

fraction of the total time period for which valid measuring data of the ambient air concentration is available from an analyser

3.5
calibration

operation that, under specified conditions, in a first step, establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a measurement result from an indication

Note 1 to entry: A calibration may be expressed by a statement, calibration function, calibration diagram, calibration curve, or calibration table. In some cases, it may consist of an additive or multiplicative correction of the indication with associated measurement uncertainty.

Note 2 to entry: Calibration should not be confused with adjustment of a measuring system, often mistakenly called “self-calibration”, nor with verification of a calibration.

[SOURCE: JCGM 200:2012 (VIM), modified, 3rd note has been deleted]

3.6
carry-over (memory effect)

influence of the previous measurement due to the retention of benzene within the instrument

3.7
certification range

concentration range for which the analyser is type approved

3.8
check

verification that the analyser is still operating within specified performance limits

3.9
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: ISO/IEC Guide 98-3:2008]

3.10
coverage factor

numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty

[SOURCE: ISO/IEC Guide 98-3:2008]

3.11
competent body

body which has been designated for a specific task (type approval tests and/or QA/QC activities in the field) by the competent authority in the Member States

3.12
detection limit

smallest concentration of a measurand that can be reliably detected by a specific measurement process

Note 1 to entry: The detection limit is calculated as $3{,}3x(sr_z/B)$, where sr_z is the standard deviation of instrument response at zero measurand concentration and B is the slope of the calibration function [5].

Note 2 to entry: In principle, the response of the instruments described in this standard to a zero concentration of benzene should be zero. Consequently, sr_z may be determined by repeatedly measuring a low concentration of benzene, e.g., 10 % of the level of the annual limit value (see 8.4.4).

3.13
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 defined by the expanded uncertainty requires explicit or implicit assumptions regarding the probability distribution characterized by the measurement result and its combined standard uncertainty. The level of confidence that may be attributed to this interval can be known only to the extent to which such assumptions may be justified.

[SOURCE: ISO/IEC Guide 98-3:2008]

Note 3 to entry: For the purpose of this standard the expanded uncertainty is the combined standard uncertainty multiplied by a coverage factor k=2 resulting in an interval with a level of confidence of 95 %.

3.14
independent measurement

individual measurement that is not influenced by a previous individual measurement

3.15
individual measurement
measurement over a time period equal to the cycle time of the analyser

Note 1 to entry: Cycle time is defined as the time taken for the analyser to complete all the required functions to report a single measurement. This may include some or all of the following: sample collection, sample trapping, sample desorbing, chromatographic analysis, analyser preparation for next measurement cycle.

3.16
influence quantity
quantity that is not the measurand but that affects the result of the measurement

[SOURCE: ISO/IEC Guide 98-3:2008]

3.17
interferent
component of the air sample, excluding the measured constituent, that affects the output signal

3.18
lack of fit
maximum deviation from the linear regression line of the average of a series of measurement results at the same concentration

3.19
limit value
level fixed on the basis of scientific knowledge, with the aim of avoiding, preventing or reducing harmful effects on human health and/or the environment as a whole, to be attained within a given period and not to be exceeded once attained

[SOURCE: 2008/50/EC [1]]

3.20
long term drift
difference between zero or span readings over a determined period of time (e.g. period of unattended operation)

3.21
monitoring station
enclosure located in the field in which an analyser has been installed to monitor concentrations of one or more ambient air pollutants in such a way that its performance and operation complies with the prescribed requirements

3.22
parallel measurements
measurements from analysers of same type and model, sampling from one and the same sampling manifold starting at the same time and ending at the same time

3.23
performance characteristic
one of the parameters assigned to equipment in order to define its performance

3.24
performance criterion

limiting quantitative numerical value assigned to a performance characteristic, to which conformance is tested

3.25
period of unattended operation

time period over which the drift complies with the performance criterion for long term drift

3.26
repeatability (of results of measurement)

closeness of the agreement between the results of successive individual measurements of benzene carried out under the same conditions of measurement

Note 1 to entry: These conditions include:

- the same measurement procedure;
- the same observer;
- the same analyser, used under the same conditions;
- at the same location;
- repetition over a short period of time.

3.27
reproducibility under field conditions

closeness of the agreement between the results of simultaneous measurements with two analysers in ambient air carried out under the same conditions of measurement

Note 1 to entry: These conditions are called field reproducibility conditions and include:

- the same measurement procedure;
- two identical analysers, used under the same conditions;
- at the same monitoring station;
- the period of unattended operation.

3.28
sampled air

ambient air that has been sampled through the sampling inlet and sampling system

3.29
sample gas temperature

temperature of the sampled gas at the sample inlet outside the monitoring station

3.30
sampling device

component of the analyser which samples an accurately known volume of ambient air

Note 1 to entry: For the purpose of this European Standard, typical devices may consist of a mass-flow controller and timed switching valve, or a sampling syringe.

3.31
sampling system
assembly of components needed to transfer the sampled air to the analyser

3.32
short-term drift
difference between zero or span readings at the beginning and end of a 12-hour period

3.33
standard uncertainty
uncertainty of the result of a measurement expressed as a standard deviation

[SOURCE: ISO/IEC Guide 98-3:2008]

3.34
surrounding temperature
temperature of the air directly surrounding the analyser (temperature inside the monitoring station or laboratory)

3.35
type approval
decision taken by a competent body that the pattern of an analyser conforms to specified requirements

3.36
type approval test
examination of two or more analysers of the same pattern which are submitted by a manufacturer to a competent body including the tests necessary for approval of the pattern

3.37
uncertainty (of measurement)
parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand

[SOURCE: ISO/IEC Guide 98-3:2008]

4 Abbreviated terms

AMS	automated measuring system
MFC	mass flow controller
PTFE	polytetrafluoroethylene
QA	quality assurance
QC	quality control

5 Principle

5.1 General

This European Standard describes the method for measurement of the concentration of benzene in ambient air by means of automated sampling and analysis by gas chromatography (GC). The requirements, the specific components of the GC analyser and its sampling system are described. A number of performance characteristics with associated minimum performance criteria are given for the analyser. The actual values of these performance characteristics for a specific type of analyser shall be determined in a so-called type approval test for which procedures have been described. The type approval test comprises a laboratory and a field test. The selection of a type approved analyser for a specific measuring task in the field is based on the calculation of the expanded uncertainty of the measurement method. In this expanded uncertainty calculation the actual values of various performance characteristics of a type approved analyser and the site-specific conditions at the monitoring station are taken into account (see 9.6). The expanded uncertainty of the method shall not exceed 25 % for fixed measurements or 30 % for indicative measurements, as specified in Annex I of Directive 2008/50/EC. Requirements and recommendations for quality assurance and quality control are given for the measurements in the field (see 9.4).

5.2 Measuring principle

A measured volume of sample air is drawn or forced through a sampling trap (sorbent tube). Provided suitable sorbents are chosen, benzene is retained by the sorbent tube and is quantitatively removed from the flowing air stream. The collected benzene is desorbed by heat and is transferred by inert carrier gas into a gas chromatograph equipped with a capillary column and a suitable detector (see 7.6), where it is analysed. Prior to entering the column the sample may be concentrated either on a cryo-trap, which is heated to release the sample into the column, or on a pre-column, where higher boiling hydrocarbons are removed from the pre-column by back flush.

Two general types of instruments are used. One type samples for only part of the time in each cycle whereas the other type of instrument samples continuously as illustrated in Figures 1 and 2 respectively. Typical cycle times are between 15 min and 1 h.

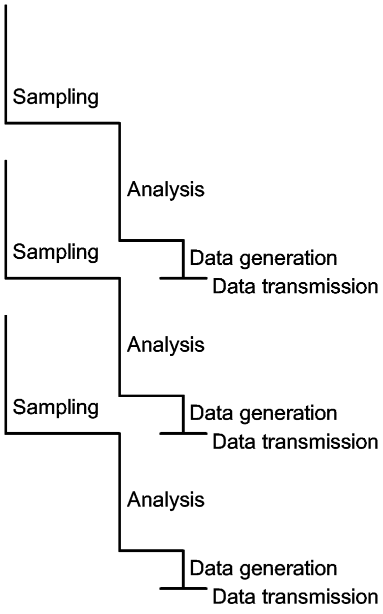


Figure 1 — Sampling by single trap

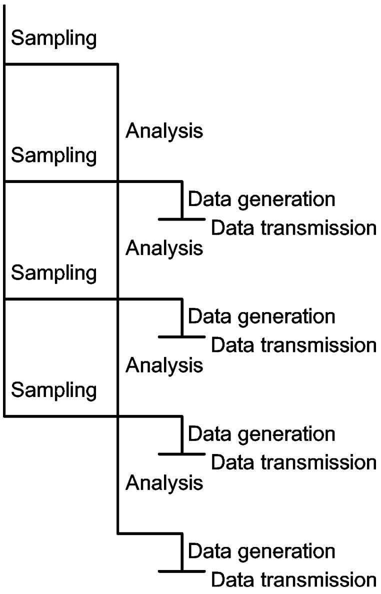


Figure 2 — Sampling by multi-trap

Special attention has to be paid to gases that may co-elute with benzene on the chromatographic column selected, such as hydrocarbons with similar boiling points.

The final results for reporting shall be expressed in µg/m^3 using standard conversion factors (see Clause 10).

5.3 Type approval test

The type approval test 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 analysers in a laboratory and the same analysers in the field operated in parallel in both cases. The type approval laboratory tests shall not include the sampling inlet or sampling manifold and external data acquisition system, but shall include analyser sampling line and filter. The type approval field test may include a sampling inlet and a sampling manifold. However, the influence of these components on the test results shall be minimized by proper maintenance.

A competent body shall perform these tests. The evaluation for type approval of an analyser is based on the calculation of the expanded uncertainty in the measuring result based on the numerical values of the tested performance characteristics and compared with a prescribed maximum uncertainty.

The type approval of an analyser and subsequent QA and QC procedures provide evidence that the defined requirements concerning data quality laid out in Annex I of Directive 2008/50/EC [1] can be satisfied.

Appropriate experimental evidence shall be provided by:

— type approval tests performed under conditions of intended use of the specified method of measurement, and

— calculation of expanded uncertainty of results of measurement by reference to ISO/IEC Guide 98-3:2008.

5.4 Field operation and quality control

Prior to the installation and operation of a type approved analyser at a monitoring station, an expanded uncertainty calculation shall be performed with the actual values of the performance, obtained during the type approval tests, and the site-specific conditions at that monitoring station. This calculation shall be used to demonstrate the suitability of a type-approved analyser under the actual conditions present at that specific monitoring station.

After the installation of the approved analyser at the monitoring station its correct functioning shall be tested.

Requirements for quality assurance and quality control are given for the operation and maintenance of the sampling system, as well as for the analyser, to ensure that the uncertainty of subsequent measurement results obtained in the field is not compromised.

6 Sampling equipment

6.1 General

Depending on the installation of the analyser at a monitoring station, a single sampling line for the analyser may be chosen. Alternatively, sampling can take place from a common sampling inlet with a sampling manifold to which other analysers and equipment may be attached. Conditions and layout of the sampling system will contribute to the uncertainty of the measurement; to minimize this contribution to the expanded uncertainty, requirements for the sampling equipment are given in the following subclauses.

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

6.2 Sampling location

The location where the ambient air shall be sampled and analysed is not specified as this depends strongly on the category of a monitoring station (such as measurements in, e.g. a rural area or urban background area). Guidance and criteria on sampling points on a micro scale are given in Annex III of Directive 2008/50/EC.

6.3 Sampling system

6.3.1 Construction

The sampling system 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 analyser;
- a sampling pump in case a sampling manifold is used.

The sample inlet shall be constructed in such a way that ingress of rainwater into the sampling line or manifold is prevented. The sampling line or manifold shall be as short as practical to minimize the residence time (i.e. within 6 s, see Annex D).

In the case where a sampling manifold is used, an additional pump is necessary with sufficient capacity to fulfil the sampling requirements stated in the previous subclauses (see also 6.5 and Annex D).

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.

NOTE In practice, the best materials to be used are borosilicate glass and stainless steel.

The sampling line or manifold may be moderately heated to avoid condensation. Condensation may occur in the case of high ambient temperature and/or humidity.

The influence on the measured concentrations of the pressure drop along the sampling inlet and line or manifold and the particle filter shall be ≤ 1,0 %.

6.3.2 Particle filter

A particle filter shall be used to protect the analyser. The filter shall retain all particles likely to alter the performance of the analyser. The material of the filter and its housing shall be chemically inert to benzene.

NOTE 1 A pore size of the filter of 5 μm 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 at least every year. Overloading of the filter may cause loss of benzene by adsorption on the particle matter and may increase the pressure drop in the sampling line.

6.3.3 Loss of benzene

Depending on the location of the particulate filter, the sampling system can be contaminated by deposition of dust. This can induce losses of benzene. The sampling system shall be cleaned (as stated in 9.4.1) with a frequency which is dependent on the site-specific conditions.

6.3.4 Conditioning

The sampling system and the particle filter shall be conditioned (at initial installation and after each cleaning) to avoid temporary decreases in the measured benzene concentrations by sampling ambient air for a period of at least 30 min at the nominal sample flow rate.

These conditioning periods shall not be included in the calculation of the availability of the analyser during the type approval test (8.5.7). Conditioning may also be done in the laboratory before installing.

NOTE Conditioning during field operation is considered a part of normal maintenance. Consequently, the concentrations measured during conditioning need not be included in the calculation of data capture, and annual averages.

6.4 Control and regulation of sample volume

The volume of air sampled into the sampling trap shall be maintained within the specifications of the manufacturer of the analyser.

6.5 Sampling pump for the manifold

When a sampling manifold is used, a pump is necessary for sampling ambient air and suction of the sampled air through the sampling manifold. The inlet of the sampling pump (or blower) for the sampling manifold shall be located at the end of the sampling manifold (see Annex D). The sampling pump or fan shall have sufficient rating to ensure that all analysers connected to the manifold are supplied with the required amount of air. To verify functioning of this pump, it is recommended to install a flow alarm system. An example of a sampling manifold is given in Annex D.

The influence of the pressure drop induced by the manifold sampling pump on the measured concentration shall be ≤ 1,0 %.(see 9.6.3.1)

7 Analyser equipment

7.1 General

Annex C lists typical types of automated gas-chromatographic analysers together with their operational parameters.

The automated gas-chromatographic analyser consists of the principal components that are described in 7.2 to 7.7.

7.2 Sampling trap

A typical sampling trap is made of stainless steel or borosilicate glass. It is packed with a sorbent or series of sorbents capable of quantitatively retaining benzene in a minimum volume of air sampled needed to measure concentrations of benzene at or below 10 % of the level of the annual limit value.

A sorbent particle size of 0,18 mm to 0,25 mm (60 mesh to 80 mesh) is recommended.

The sampling trap will degrade over time due to its repetitive heating and cooling, and shall be changed in accordance with the manufacturer’s recommendations.

7.3 Sampling device

The sampling device used may vary between instruments but shall be able to deliver a known sample volume at standard conditions of temperature and pressure.

7.4 Thermal desorption unit

Depending on the instrument used the thermal desorption unit may be suitable for single- or two-stage desorption of the benzene from the sampling trap. Desorption is effected by heating the trap within a short time period whilst passing a flow of carrier gas (typically nitrogen). Temperature, gas flow rate and time need to be sufficient to quantitatively transfer the trapped benzene to a secondary trap, a pre-column or the analytical column, depending on the instrument.

When a secondary trap or pre-column are used similar requirements hold for desorption of benzene from these traps. In addition, the secondary desorption shall be such that the chromatographic resolution of benzene from (potential) interferents is optimized.

7.5 Separation unit

The separation unit consists of an analytical (separation) column and an oven used for heating the column to effect the separation of benzene from (potential) interferents within a period sufficient to allow its quantification at concentrations equal to or lower than 10 % of the annual limit value.

NOTE Effective separation and quantification may require the application of temperature programming. This will affect the minimum cycle time between measurements.

7.6 Detector

The detector shall be able to allow quantification of benzene at concentrations equal to or lower than 10 % of the annual limit value. Detectors mostly used are flame ionization and photo-ionisation detectors.

NOTE The latter does not require additional gases for its operation, but is prone to a higher response drift and requires more frequent maintenance.

7.7 Data processing system

The analyser will be equipped with software allowing the identification and quantification of benzene in the acquired chromatograms. The software shall allow for data reprocessing after acquisition, e.g., in case drift of retention windows leading to faulty identification of components.

Data processing and reprocessing may be performed at the site using a computer internal to the analyser, or using an external computer.

In case of internal data treatment, the software version should be clearly identified in the test report, as part of the unambiguous AMS designation (see 11.1).

Any data processing system associated by the manufacturer with his AMS should be considered as part of the analyser.

8 Type approval of benzene analysers

8.1 General

The determination of the concentration of benzene in ambient air has to fulfil the requirement of a maximum uncertainty in the measured values, which is prescribed by Annex I of Directive 2008/50/EC (25 % for fixed measurements or 30 % for indicative measurements). In order to achieve an uncertainty less than (or equal to) this required uncertainty, the analyser has to fulfil all the criteria for a number of performance characteristics, which are given in this standard. The values of the selected performance characteristics shall be evaluated by means of laboratory and field tests. By combining the values of the selected performance characteristics in the expanded uncertainty calculation a judgement can be made whether or not the analyser meets the criterion of maximum uncertainty prescribed by Annex I of Directive 2008/50/EC (25 % for fixed measurements or 30 % for indicative measurements).

This process of assessment (type approval test) of the values of the performance characteristics comprises laboratory and field tests and the calculation of the expanded uncertainty. At least two analysers of the same type shall be tested in the laboratory. The same analysers shall be tested during the field test. All analysers tested shall pass both tests.

The type approval procedure shall fulfil the certification requirements laid down in European Standards EN 15267-1 and EN 15267-2. A competent body shall perform the type approval tests. The type approval shall be awarded by or on behalf of the competent authority. The competent body performing the required tests shall be able to demonstrate that it works in compliance with the requirements of internationally accepted standards for test laboratories.

NOTE 1 EN ISO/IEC 17025 is a harmonized internationally accepted standard.

NOTE 2 An accreditation by a member body of the European co-operation for Accreditation to EN ISO/IEC 17025 is a demonstration of compliance.

EN 15267-1 specifies the general principles of the product certification of automated measuring systems (AMS) for monitoring emissions from stationary sources and ambient air quality. This product certification consists of the following sequential stages:

— performance testing of an AMS;

— initial assessment of the AMS manufacturer’s quality management system;

— certification;

— post-certification product-surveillance.

EN 15267-2 covers the supplementary requirements for an AMS manufacturer’s management system to EN ISO 9001 for the control of design and manufacturing of AMS. This European Standard also serves as a reference document for auditing the AMS manufacturer’s management system.

8.2 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. When type-approval tests are performed on analysers with other certification ranges, the performance criteria stated in absolute units such as nmol/mol/K shall be adjusted. All criteria expressed in relative units (e.g. %) shall remain the same.

The determination of the value of the performance characteristics stated in Table 1 shall be performed by a competent body during the laboratory test and field test according to the procedures described in 8.4, 8.5 and Annex A.

Table 1 — Relevant performance characteristics and criteria

No.	Performance characteristic	Symbol	Section	Lab. Test	Field test	Performance criterion for benzene
1	Repeatability standard deviation at 10 % of the level of the annual limit	s_{rz}	8.4.4	x		≤ 0,20 µg/m^3
2	Repeatability standard deviation at the level of the annual limit value	$s_{r,ct}$	8.4.4	x		≤ 0,25 µg/m^3
3	Lack of fit (residual from the linear regression function)		8.4.5			
3a	Largest residual from the linear regression function at concentrations higher than zero	r_{max}		x		≤ 5,0 % of the measured value
3b	Residual at zero	r_z		x		≤ 0,50 µg/m^3
4	Sensitivity coefficient of sample gas pressure	b_{gp}	8.4.6	x		≤ 0,10 µg/m^3/kPa
5	Sensitivity coefficient of surrounding temperature	b_{st}	8.4.7	x		≤ 0,08 µg/m^3/K
6	Sensitivity coefficient of electrical voltage	b_V	8.4.8	x		≤ 0,08 µg/m^3/V
7	Interferents at concentration c_t (at a level of the annual limit)		8.4.9			
7a	H_2O with concentration 19 mmol/mol [b]	$b_{H2O,ct}$		x		≤ 0,015 µg/m^3/(mmol/mol)
7b	Organic compound mixture [d]	Δx_{OC}		x		≤ 0,25 µg/m^3
8	Carry over (memory effect)	c_m	8.4.10	X		≤ 1,0 µg/m^3 as the response when measuring zero gas after test gas
9	Reproducibility standard deviation under field conditions	$S_{r,f}$	8.5.5		x	≤ 0,25 µg/m^3 as the average of a three month period
10	Long-term drift					
10a	Long-term drift at zero	$D_{l,z}$	8.5.4		x	≤ 0,5 µg/m^3

No.	Performance characteristic	Symbol	Section	Lab. Test	Field test	Performance criterion for benzene	
10b	Long-term drift at span level [a]	$D_{l,s}$	8.5.4		x	≤ 10	% of maximum of certification range
11	Short-term drift at span level [a]	$D_{s,s}$	8.4.3	X		≤ 2,0	µg/m³ over 12 h
12	Difference sample/calibration port [c]	Δx_{sc}	8.4.11	X		≤ 1,0	%
13	Period of unattended operation		8.5.6		x	14	Days
14	Availability of the analyser	A_a	8.5.7		x	> 90	%

[a] Span level is around 70 % to 80 % of the certification range.

[b] For information, a H_2O-concentration of 19 mmol/mol corresponds to 80 % RH at 20 °C and 101,3 kPa.

[c] If relevant.

[d] This shall then be excluded from the uncertainty budget.

8.3 Design changes (EN 15267-1 and EN 15267-2)

The manufacturer shall evaluate all changes to a type-approved analyser. The manufacturer shall document all changes and evaluations in accordance with the requirements of EN 15267-1 and EN 15267-2 in such a way that they can be audited.

NOTE See also EN ISO 9001 [4].

When the manufacturer makes design changes, the manufacturer shall notify the test laboratory and relevant body unless the manufacturer has evidence to show that the analyser still meets the performance stated in the original analyser certificate. The following three classes of changes to type-approved analyser are defined:

- Type 0: changes that have no measurable influence to the performance of the analyser;
- Type 1: changes that can have an influence on the performance of the analyser, but where subsequent tests prove that such changes do not have a significant influence;
- Type 2: changes that have a significant influence on the performance of the analyser.

A significant influence reduces the performance of the analyser compared to that recorded in the certificate for the stipulated performance characteristics. When the manufacturer makes Type 2 changes to the analyser, the test laboratory in consultation with the Competent Authority shall determine whether supplementary or complete retesting is required to maintain type approval. Where Type 2 changes are identified, further evaluation shall be carried out by a test laboratory in liaison with the relevant body.

8.4 Procedures for determination of the performance characteristics during the laboratory test

8.4.1 General

A competent body shall perform the determination of the performance characteristics in the laboratory as a part of the type approval test. The quality of the materials and equipment used in the described test procedures shall be in accordance with the requirements given in this European Standard. The tests shall be performed on at least two analysers.

8.4.2 Test conditions

8.4.2.1 General

Before operating the analyser, the operating instructions of the manufacturer shall be followed particularly with regard to the set-up of equipment and the quality and quantity of the consumable products necessary.

The analyser should be allowed to warm up during the time specified by the manufacturer before undertaking any tests. If the warm-up time is not specified, a minimum of 4 h is recommended.

If an auto-rescaling function or self-correction function are considered “normal operational condition”, then the times and magnitudes of any self-correction shall be available to the test laboratory. The magnitude of the auto zero and the auto span drift corrections both have the same restrictions as laid down in the performance characteristics (see 8.4.3).

When applying test gases to the analyser, the test gas system shall be operated sufficiently long before starting the tests in order to stabilize the concentrations applied to the analyser. The analyser shall be tested with the particle filter installed.

During laboratory tests for the type approval the settings of the monitor shall be as the manufacturer requires. All settings shall be noted down in the test report.

8.4.2.2 Parameters

During the test for each individual performance characteristic, the values of the following parameters shall be stable within the specified range given in Table 2.

Table 2 — Set points and stability of test parameters

Parameter	Set points	Stability
Sample gas pressure	Manufacturer’s specification (except for the sample gas pressure test, see 8.4.6)	± 0,2 kPa
Surrounding air temperature	20 °C to 23 °C (except for the temperature of the surrounding air test, see 8.4.7)	± 2 K
Electrical voltage[a]	At nominal line voltage and within manufacturer’s specifications (except for the voltage dependence test, see 8.4.8)	± 1 %
Sample volume	Manufacturer’s specification	± 1 %

[a] For an analyser operating on direct current the type approval test of voltage variation shall be carried out over the range of ± 10 % of the nominal voltage.

8.4.2.3 Test gases

For the determination of the various performance characteristics, test gases traceable to (inter)nationally accepted standards shall be used unless otherwise stated in this standard. Methods for the generation of test gases are given in Table 3.

Table 3 — Methods for preparation of test gases

Method	Description	Traceability/ Standard to be used
Cylinder	Gas cylinder (benzene gas mixture in nitrogen)	EN ISO 6142 EN ISO 6143
Dynamic preparation	Dynamic dilution of benzene gas mixtures – From cylinders – From continuous injection, diffusion, saturation or permeation devices	EN ISO 6145-4 EN ISO 6145-6 EN ISO 6145-7 EN ISO 6145-8 EN ISO 6145-9 or EN ISO 6145-10
Static dilution	Preparation by means of injecting known amounts of benzene into a known volume of air	EN ISO 6144

Possible contamination of zero and test gas shall not significantly influence the results of the laboratory tests. Therefore the test gases and zero gas shall meet the following specifications:

— tolerances in the concentrations of the test gases used (except for benzene at 10 % of the limit value): ± 10 %; for benzene at the level of 10 % of the limit value: ± 40 %.

— maximum permitted expanded uncertainties (95 % confidence) in the concentration of gases used for laboratory tests: 5 %.

Specifications of the purity of test gases and zero gas (expressed as absolute value) are given in Table 4 to Table 6.

Table 4 — Specification for purity of test gas

Pollutant	Concentration
Sum of organic compounds other than benzene (see 8.4.9)	≤ 1 µg/m³
Water	≤ 150 µmol/mol

NOTE Certain specific organic compounds may be deliberately included in the test gas. In this case, the purity specification excludes these.

Table 5 — Specification for purity of zero gas for interferents testing

Pollutant	Concentration
Benzene	≤ 0,10 µg/m³
Sum of organic compounds other than benzene (see 8.4.9)	≤ 1 µg/m³
Water	≤ 150 µmol/mol

Table 6 — Specification for purity of zero gas for other tests

Pollutant	**Concentration**
Benzene	≤ 0,10 µg/m^3
Sum of organic compounds other than benzene (see 8.4.9)	≤ 10 µg/m^3
Water	≤ 150 µmol/mol

It is advised to perform the field tests with the same set of cylinders and zero air generators, exclusively reserved for the tests. The stability of both the zero air and the test gas should be guaranteed over a period longer than the test period.

8.4.3 Short-term drift

After the required stabilization period (8.4.2.1), the analyser shall be adjusted at span level (around 70 % to 80 % of the maximum of the certification range of benzene). Perform 5 successive measurements; calculate the average of the last 4 measurements.

The analyser shall be kept running under the laboratory conditions (8.4.2.2) whilst analysing ambient air. After a period of 12 h test gas is fed to the analyser. Perform 5 successive measurements; calculate the average of the last 4 measurements.

The short-term drift at span level shall be calculated as follows:

$$D_{\mathrm{s,s}} = x_{\mathrm{s,2}} - x_{\mathrm{s,1}} \tag{1}$$

where

$D_{\mathrm{s,s}}$ is the 12-hour drift at span in µg/m^3;

$x_{\mathrm{s,1}}$ is the average concentration of the measurements at span level at the beginning of the drift period in µg/m^3;

$x_{\mathrm{s,2}}$ is the average concentration of the measurements at span level at the end of the drift period in µg/m^3.

$D_{\mathrm{s,s}}$ shall comply with the performance criterion in Table 1.

8.4.4 Repeatability standard deviation

After the required stabilization period (8.4.2.1), the analyser shall be adjusted at span level (around 70 % to 80 % of the maximum of the certification range of benzene).

Eleven successive measurements shall be performed at test gas concentrations at 10 % of the level of the annual limit value and at the level of the annual limit value.

From the last 10 results of these measurements the repeatability standard deviations (s_{r}) at 10 % of the annual limit value and at the annual limit value shall be calculated according to:

$$s_r = \sqrt{\frac{\sum\left(x_i - \overline{x}\right)^2}{n-1}} \tag{2}$$

where

s_{r} is the repeatability standard deviation in µg/m^3;

x_i is the result of the ith measurement in µg/m^3;

$\overline{x}$ is the average of the 10 measurements in μg/m^3;

n is the number of measurements, n =10.

s_r shall comply with the performance criterion in Table 1, both at 10 % of the annual limit value and at the annual limit value.

The repeatability standard deviation at 10 % of the annual limit value is used in combination with the slope of the calibration function determined in 8.4.5 to calculate the detection limit of the analyser as [5]:

$$l_{\text{det}} = 3{,}3 \cdot \frac{s_{r,z}}{B} \tag{3}$$

where

l_{det} is the detection limit of the analyser in μg/m^3;

$s_{\text{r,z}}$ is the repeatability standard deviation at 10 % of the annual limit value in μg/m^3;

B is the slope of the calibration function determined according to Annex A using the data from 8.4.5.

8.4.5 Lack of fit of linearity of the calibration function

The lack of fit of linearity of the calibration function of the analyser shall be tested over the range of 0 % to 90 % of the maximum of the certification range of benzene, using at least six concentrations (including the zero point). The analyser shall be adjusted at a concentration of about 50 % of the maximum of the certification range. At each concentration (including zero) at least four individual measurements shall be performed. The first measurement of each series shall be excluded from the calculation of the regression function.

The concentrations shall be applied in the following sequence: 50 %, 10 %, 30 %, 5%, 90 % and 0 %. After each change in concentration the first measurement result shall be discarded.

The uncertainty in the dilution ratios for the applied concentrations shall be less than 1,5 % with respect to each other.

NOTE The design of the test (number of concentrations and number of repetitions) is such that the deviation from a linear function can be determined with sufficient accuracy. The test is also sufficiently robust to detect the case of non-linearity in the range from zero to some concentration at the lower end of the range as well as non-linearity from that lower end of the range to the higher end of the range.

Calculation of the linear regression function and residuals shall be performed according to Annex A. All the (relative) residuals from the linear regression function shall fulfil the criteria as stated in Table 1.

The largest value of the relative residuals is reported as r_{max} and shall be taken into account in demonstrating compliance with type approval requirement (a). This value of the relative residual value shall be taken in the calculation of type approval requirement (b) and (d) at the level of the annual limit value (see 8.6).

8.4.6 Sensitivity coefficient to sample gas pressure

Perform 5 successive measurements at span level (around 70 % to 80 % of the maximum of the certification range of benzene) at an absolute pressure of about 80 kPa ± 0,2 kPa and at an absolute pressure of about 110 kPa ± 0,2 kPa. Calculate the average of the last 4 measurements for each pressure.

The sample gas pressure influence is calculated by:

$$b_{\mathrm{gp}}=\left|\frac{\left(x_{P2}-x_{\mathrm{P1}}\right)}{\left(P_2-P_1\right)}\right| \tag{4}$$

where

b_{gp} is the sample gas pressure sensitivity coefficient in µg/m³/kPa;

x_{P1} is the average concentration of the measurements at sampling gas pressure P_1 in µg/m³;

x_{P2} is the average concentration of the measurements at sampling gas pressure P_2 in µg/m³;

P_1 is the minimum sampling gas pressure in kPa;

P_2 is the maximum sampling gas pressure in kPa.

b_{gp} shall comply with the performance criterion in Table 1.

8.4.7 Sensitivity coefficient to the surrounding temperature

The sensitivity of the analyser readings to the surrounding temperature shall be determined by performing measurements at the following temperatures (or within the specifications of the manufacturer):

a) at a minimum temperature $T_{\mathrm{S},1}$ = 0 °C;

b) at a maximum temperature $T_{\mathrm{S},2}$ = 30 °C.

For these tests a climate chamber is necessary.

At each temperature setting the criteria for warm-up or stabilization time are to be met according to 8.4.2.1.

This test shall be carried out by using a test gas mixture (around 70 % to 80 % of the maximum of the certification range). The analyser shall be adjusted at this level at the prescribed nominal test temperature (see Table 2).

Five successive measurements are performed at each temperature. The results of the first measurement at each temperature shall be discarded.

The sensitivity coefficient for surrounding temperature dependence is calculated as:

$$b_{\mathrm{st}}=\left|\frac{\left(x_2-x_1\right)}{\left(T_{S,2}-T_{s,1}\right)}\right| \tag{5}$$

where

b_{st} is the surrounding air temperature sensitivity coefficient span in µg/m³/K;

x_1 is the average of the measurements at $T_{\mathrm{S},1}$ in µg/m³;

x_2 is the average of the measurements at $T_{\mathrm{S},2}$ in µg/m³;

$T_{\mathrm{S},1}$ is the minimum surrounding air temperature in °C;

$T_{\mathrm{S},2}$ is the maximum surrounding air temperature in °C.

b_{st} shall comply with the performance criterion in Table 1.

A prerequisite is that the values of x_1 and x_2 shall not differ by more than 2,5 µg/m³ from the level measured when adjusting the analyser.

8.4.8 Sensitivity coefficient to electrical voltage

The sensitivity coefficient of electrical voltage shall be determined at both ends of the specified voltage range, V_1 and V_2 at a concentration around 70 % to 80 % of the maximum of the certification range of benzene. Perform 5 successive measurements at each voltage; calculate the average of the last 4 measurements.

The voltage dependence is calculated from:

$$b_\mathrm{v} = \left| \frac{\left(x_{\mathrm{V}_2} - x_{\mathrm{V}_1} \right)}{\left(V_2 - V_1 \right)} \right| \qquad (6)$$

where

b_v is the voltage sensitivity coefficient in µg/m³/V;

x_{V_1} is the average concentration reading of the measurements at voltage V_1 in µg/m³;

x_{V_2} is the average concentration reading of the measurements at voltage V_2 in µg/m³;

V_1 is the minimum voltage in V specified by the manufacturer;

V_2 is the maximum voltage in V specified by the manufacturer.

b_v shall comply with the performance criterion in Table 1.

For an analyser operating on direct current the type approval test of voltage variation shall be carried out at ± 10 % of the nominal voltage.

8.4.9 Interferents

8.4.9.1 General

The analyser response to certain interferents, which are to be expected to be present in ambient air, shall be tested. The interferents can give a positive or negative response. The test shall be performed at a test concentration (c_t) of benzene similar to the annual limit value.

The concentrations of the mixtures of the test gases with the interferent shall have an expanded uncertainty of ≤ 10 % and shall be traceable to (inter)nationally accepted standards.

A correction on the concentration of the measurand shall be made for the dilution effect due to addition of an interferent (e.g. water vapour).

After adjustment of the analyser at span level the analyser shall be fed with a test gas with a concentration (c_t) of benzene similar to the annual limit value. With this mixture 3 measurements shall be performed, of which the results of the last two shall be used. This procedure shall be repeated with a mixture of benzene at concentration c_t and the interferent to be investigated.

8.4.9.2 Water vapour

The influence of water vapour shall be tested at a concentration of 19 mmol/mol. The sensitivity coefficient at the benzene test gas concentration c_t is calculated as:

$$\mathrm{b}_{\mathrm{H2O}} = \frac{\mathrm{x}_{+w} - x_{-w}}{\mathrm{c}_\mathrm{w}} \qquad (7)$$

where

b_{H2O} is the sensitivity coefficient to water vapour at concentration c_t, in µg/m³/(mmol/mol)

x_{+w} is the average of the measurements at concentration c_t in the presence of water vapour, in µg/m³;

x_{-w} is the average of the measurements at concentration c_t in the absence of water vapour, in µg/m³;

c_w is the water vapour test gas concentration, in mmol/mol.

The sensitivity coefficient shall comply with the performance criterion in Table 1.

8.4.9.3 Organic compounds

The interference test with the organic compound mixture is a test to ensure that the contributions to the signal of benzene of organic compounds that may co-elute with benzene are insignificant. The results of the test (Formula (8)) shall comply with the performance criterion in Table 1.

$$\Delta x_{oc} = x_{+} - x_{-} \tag{8}$$

where

Δx_{oc} is the contribution of the organic compound mixture to the signal of benzene, in in µg/m³;

x_{+} is the average of the response measured for benzene at concentration c_t (at the level of the annual limit value) in the presence of the interferents, in µg/m³;

x_{-} is the average of the response measured for benzene at concentration c_t (at the level of the annual limit value) in the absence of the interferents, in µg/m³.

One of the methods described in Table 3 shall be used for the preparation of the test-gas-mixture with known concentrations as listed in Table 7.

Table 7 — Organic compound mixture for interferents testing

Compound	Concentration
Methylcyclopentane	5 µg/m³
2,2,3-Trimethylbutane	5 µg/m³
2,4-Dimethylpentane	5 µg/m³
2,2,4-Trimethylpentane	5 µg/m³
Cyclohexane	5 µg/m³
2,3-Dimethylpentane	5 µg/m³
2-Methylhexane	5 µg/m³
3-Ethylpentane	5 µg/m³
Trichloroethene	5 µg/m³
1-Heptane	5 µg/m³
1-Butanol	5 µg/m³

NOTE The compounds listed in Table 7 are typical interferents that may be encountered in practice. However, compounds such as carbon tetrachloride or butanol may be present under site-specific conditions. In such cases, the responsibility for proper determination of benzene lies with the network operating the analyser by proper choice of separation conditions (analytical column; column temperature program).

8.4.10 Carry over (memory effect)

The retention of benzene in the measurement system after the performance of a measurement (carry over) is determined by applying a high concentration level (around 90 % of maximum of the certification range of benzene) followed by zero air.

At the high concentration level two successive measurements shall be performed, after which the gas supply is switched to zero air. The result of the subsequent measurement of the zero air is used to calculate the concentration of benzene c_m resulting from carry over.

The test sequence shall be repeated at least 3 times. The average of the results for c_m shall be reported and shall fulfil the criterion in Table 1.

NOTE This test is optimally carried out by synchronizing the injection of the test gas with the beginning of the sampling time of the analyser.

8.4.11 Difference sample/calibration port

If the analyser has different ports for feeding sample gas and calibration gas the difference in response of the analyser to feeding through the sample or calibration port shall be tested. The test shall be carried out by feeding the analyser with a test gas with a concentration of around 70 % to 80 % of the maximum of the certification range of benzene through the sample port. For each port 5 consecutive measurements shall be performed, of which the last 4 results shall be used. The difference shall be calculated according to:

$$\Delta x_{\mathrm{sc}} = \frac{x_{\mathrm{sam}} - x_{\mathrm{cal}}}{c_{\mathrm{t}}} \times 100 \tag{9}$$

where

Δx_{sc} is the difference sample/calibration port in %;

x_{sam} is the average of the measured concentration using the sample port in µg/m^3;

x_{cal} is the average of the measured concentration using the calibration port in µg/m^3;

c_{t} is the concentration of the test gas in µg/m^3.

Δx_{sc} shall comply with the performance criterion in Table 1.

8.5 Determination of the performance characteristics during the field test

8.5.1 General

The determination of the performance characteristics in the field as a part of the type approval test shall be performed by a competent body. The quality of the materials and equipment used in the described test procedures shall be in accordance with the requirements given in this standard.

In the field test during a period of three months 2 analysers are tested for availability (period of unattended operation), reproducibility in the field and long-term drift. The test shall not be interrupted. Only in exceptional cases, which shall be justified (e.g. in the case of operation-related interruptions or change of site), shorter testing periods may be included in the field test. However, the total duration of the test periods shall be at least three months.

The analysers are run in parallel at one and the same sampling point at a selected monitoring station with specific ambient air conditions (8.5.2). Operational requirements are given for the correct determination of the long-term drift and the reproducibility under field conditions (8.5.3).

8.5.2 Selection of a monitoring station for the field test

The selection of a monitoring station is based on the following criteria:

Location:

— traffic orientated station (≤ 10 m from kerb-side).

Monitoring station facilities:

— sufficient capacity of the sampling manifold;

— enough room to place two analysers with calibration gases and/or calibration facilities;

— surrounding temperature control for the analysers, climate controlled at (20 ± 4) °C with temperature registration;

— stable electrical voltage.

Other items that could be considered:

— presence of telemetry/telephone facilities for remote surveillance of the functioning of the equipment;

— accessibility.

8.5.3 Operational requirements

After installation of the analysers at the monitoring station the proper functioning of the analysers shall be tested. This comprises of (among other things) the proper connections to the sampling manifold, sample gas flows, correct operating temperatures, response to test gas, data transmission and other items which shall be judged necessary by the competent body.

After verification of the proper functioning the analysers shall be adjusted at a value of around 70 % to 80 % of the maximum of the certification range.

During the three-month period the maintenance requirements, by the manufacturer of the analyser shall be followed.

For the first 14 d, measurements with zero and test gas shall be performed at least every two days. The test gas shall have a concentration around 70 % to 80 % of the maximum of the certification range. At least four independent, successive measurements shall be performed. The results shall be recorded. For the remainder of the trial, measurements with zero and test gas shall be performed at least every two weeks.

During the three-month period no manual span adjustments shall be made to the analyser, as this will influence the determination of the long-term drift. The measurement data from the analyser shall only be corrected in a mathematical way assuming a linear drift since the last zero or span check.

If an auto-rescaling function or self-correction function is included and considered “normal operational condition”, it shall be enabled during the field tests. The magnitude of any self-correction shall be available to the test laboratory. The magnitude of the auto span drift corrections over the period of unattended operation (long-term drift) shall have the same restriction as laid down in the performance characteristics.

For the determination of the various performance characteristics, test gases (air containing a certain benzene concentration) shall be used, traceable to (inter)nationally accepted standards, unless otherwise stated in this European Standard. Various methods for the generation of test gases are given in Table 3.

The stability of the test gas used for the field tests shall be proven to be insignificant compared to the long-term drift criterion in Table 1. Possible contamination of the test gas shall not significantly influence the results of field tests. Therefore the test gas shall meet the following specifications:

- Maximum permitted expanded uncertainties in the concentration of gas used for field tests: 5 %.
- Specification of the purity of test gas and zero air used for dilution (expressed as absolute values) are given in Tables 4, 5 and 6.

It is advised to perform the field tests with the same set of cylinders, exclusively reserved for the tests. The stability of the test gas should be guaranteed over a period longer than the test period.

8.5.4 Long term drift

After each bi-weekly span check the drift of the analysers under test shall be calculated at zero and span following the procedures as given underneath. If the drift compared to the initial calibration exceeds one of the performance criteria for drift at zero or span level, the “period of unattended operation” equals the number of weeks until the observation of the infringement, minus two weeks. For further (uncertainty) calculations the values for “long term drift” are the values for span drift over the period of unattended operation.

At the beginning of the drift period five measurements are recorded at span level; the results of the first measurement shall be discarded.

The long-term drift is calculated as follows:

$$D_{\mathrm{l,z}} = (\mathrm{x}_{\mathrm{z},1} - \mathrm{x}_{\mathrm{z},0}) \tag{10}$$

where

$D_{\mathrm{l,z}}$ is the drift at zero in µg/m^3;

$x_{\mathrm{z},0}$ is the average concentration of the measurements at zero level at the beginning of the drift period (just after the initial calibration) in µg/m^3;

$x_{\mathrm{z},1}$ is the average concentration of the measurements at zero level at the end of the drift period in µg/m^3.

$D_{\mathrm{l,z}}$ shall comply with the performance criterion in Table 1.

$$D_{\mathrm{l,s}} = \frac{\left(x_{\mathrm{s},1} - x_{\mathrm{s},0}\right) - D_{\mathrm{l,z}}}{x_{\mathrm{s},1}} \times 100 \tag{11}$$

where

$D_{\mathrm{l,s}}$ is the drift at span concentration c_{t} in %;

$x_{\mathrm{s},0}$ is the average concentration of the measurements at span level at the beginning of the drift period just after the initial calibration in µg/m^3;

$x_{\mathrm{s},1}$ is the average concentration of the measurements at span level at the end of the drift period in µg/m^3;

$D_{\mathrm{l,z}}$ is the drift at zero in µg/m^3.

$D_{\mathrm{l,s}}$ shall comply with the performance criterion in Table 1.

NOTE For the determination of a systematic or random drift, a graph with test gas readings can be useful.

8.5.5 Reproducibility standard deviation under field conditions

The reproducibility standard deviation under field conditions is calculated from the measured data during the three-month period.

The difference $\Delta x_{f,i}$ for each (*i*th) parallel measurement is calculated from:

$$\Delta x_{f,i} = x_{f,1,I} - x_{f,2,i} \tag{12}$$

where

$\Delta x_{f,i}$ is the *i*th difference in a parallel measurement in µg/m³;

$x_{f,1,i}$ is the *i*th measurement result of analyser 1 in µg/m³;

$x_{f,2,i}$ is the *i*th measurement result of analyser 2 in µg/m³.

The reproducibility standard deviation under field conditions ($s_{\mathrm{r,f}}$) is calculated according to:

$$s_{r,f} = \sqrt{\frac{\sum_{i=1}^{n} \Delta x_{f,i}^{2}}{2n}} \tag{13}$$

where

$s_{\mathrm{r,f}}$ is the reproducibility standard deviation under field conditions in µg/m³;

n is the number of parallel measurements;

x_f is the average concentration of benzene measured during the field test in µg/m³.

The reproducibility standard deviation under field conditions, $s_{\mathrm{r,f}}$, shall comply with the performance criterion in Table 1.

8.5.6 Period of unattended operation

The period of unattended operation is either the time period within which the drift is within the performance criterion for long term drift, or the maintenance period specified by the manufacturer whichever is the shorter. All malfunctions during the field test shall be included in the test report.

If one of the analysers malfunctions during the field test, then the field test may be restarted to show whether the malfunction was coincidental or bad design, by agreement between the test laboratory and manufacturer.

A minimum period of unattended operation is normally recommended to be at least two weeks.

8.5.7 Period of availability of the analyser

The correct operation of the analysers shall be checked at least every 14 d. It is recommended to perform this check every day during the first 14 d. These checks consist of plausibility checks on the measured values, as well as when available status signals and other relevant parameters. Time, duration and nature of any malfunctioning shall be logged.

The total time period with useable measuring data is the period during the field test during which valid measuring data of the ambient air concentrations are obtained. In this time period the time needed for calibrations, conditioning of sampling system and filters (6.3) and maintenance shall not be included.

The availability of the analyser is calculated as:

$$A_{\mathrm{a}} = \frac{t_{\mathrm{u}}}{t_{\mathrm{t}}} \times 100 \tag{14}$$

where

A_a is the availability of the analyser;

t_u is the total time period with validated measuring data;

t_t is the time period of the field test minus the time for calibration, conditioning and maintenance.

t_u and t_t shall be expressed in the same units (e.g. hours).

The availability of each analyser shall comply with the criterion in Table 1.

8.6 Expanded uncertainty calculation for type approval

The type approval of the analyser consists of the following steps:

a) The value of each individual performance characteristic tested in the laboratory shall fulfil the criterion stated in Table 1.

b) The expanded uncertainty calculated from the standard uncertainties due to the values of the specific performance characteristics obtained in the laboratory tests shall fulfil the criterion as stated in Annex I of Directive 2008/50/EC (25 % for fixed measurements or 30 % for indicative measurements). This criterion is the maximum uncertainty of individual measurements for continuous measurements at the limit value. The relevant specific performance characteristics and the calculation procedure are given in Annex E.

c) The value of each of the individual performance characteristics tested in the field shall fulfil the criterion stated in Table 1.

d) The expanded uncertainty calculated from the standard uncertainties due to the values of the specific performance characteristics obtained in the laboratory and field tests shall fulfil the criterion as stated in Annex I of Directive 2008/50/EC (25 % for fixed measurements or 30 % for indicative measurements). This criterion is the maximum uncertainty of individual measurements for continuous measurements at the limit value. The relevant specific performance characteristics and the calculation procedure are given in Annex E.

The instrument can be type approved when all 4 requirements are met.

9 Field operation and ongoing quality control

9.1 General

When a type approved analyser has been chosen for a particular measuring task, the suitability of this analyser shall be evaluated at a specific measuring location. This shall be performed by means of a suitability evaluation described in 9.2.

The analyser shall be installed at a monitoring station in such a way that normal operation of the analyser is not compromised. This implies that the analyser is sheltered and shielded from dust, rain and snow, direct sun radiation, strong temperature fluctuations, etc. An enclosure (container or building) with temperature control or air conditioning usually fulfils these requirements. At some locations voltage stabilizers for the power supply may be considered, when voltage fluctuations are expected.

The operation of air conditioning systems may adversely affect the performance of the analyser. Due care should be taken to minimize direct output flow at the analyser and/or strong temperature fluctuations in operating air conditioning systems.

After installation of the analyser at the measuring station the analyser shall be tested for proper operation. This is described in 9.3.

Some tests may be performed either in the lab or on site.

Subsequently, once the analyser at the specific site has been judged to conform with the EU data quality objectives of Directive 2008/50/EC, quality assurance and quality control procedures for ongoing monitoring of benzene concentrations shall be followed (as described in 9.4) in order to ascertain that the measured data comply with the uncertainty requirements as given in Annex I of Directive 2008/50/EC (25 % for fixed measurements or 30 % for indicative measurements).

9.2 Suitability evaluation

9.2.1 General

When a type approved analyser has been chosen, the suitability of this analyser shall be evaluated for the site-specific conditions at the monitoring site. For example, temperature fluctuations might be such that the type approved analyser does not fulfil the uncertainty requirements under these conditions. Consequently it may be necessary to control the temperature of the air directly surrounding the analyser. Benzene test gases that are used for the calibration of the analyser shall be traceable to (inter)nationally accepted standards.

9.2.2 Analyser for a monitoring station or task

An expanded uncertainty assessment for the type-approved analyser shall be made following 9.9.The site-specific conditions which shall be estimated, are given in Table 8. The performance of the uncertainty assessment is described in Annex F.

Table 8 — Site-specific conditions to be evaluated

Parameters	**Remarks**
Sample pressure range	The range of sample gas pressures expected during a whole period of a year shall be estimated.
Surrounding air temperature range	The range of temperatures expected shall be within the range specified in the type approval test. Temperature may be controlled thermostatically.
Line voltage range[a]	The range of line voltages expected shall be within the range in the type approval test. Voltage fluctuations may be controlled by means of voltage stabilizers.
H_2O concentration range	The range of hourly-average H_2O concentrations during a whole period of a year shall be estimated.
Expanded uncertainty of the calibration gas	The expanded uncertainty of the calibration gas shall be included. This implies the uncertainty of the calibration gas itself as well as the uncertainty of any dilution system (where applicable).
Calibration frequency	The intended calibration frequency shall be used for the calculation of the influence of the drift.

[a] For an analyser operating on direct current the type approval test of voltage variation shall be carried out over the range of ± 10 % of the nominal voltage.

As a “default” input the extreme conditions from the type-approval may be used.

If the site-specific conditions are outside the conditions for which the analyser is type approved, then either:

— the analyser is subjected to supplementary tests by a competent body under these site-specific conditions;

- the analyser is tested by the network under these site-specific conditions when the number of sites under concern is limited;
- the uncertainty assessment is performed by extrapolation of the conditions under concern.

In each case the uncertainty shall be recalculated and a report shall be issued. If the analyser complies with the requirements laid down in Annex I of Directive 2008/50/EC (25 % for fixed measurements or 30 % for indicative measurements), then that particular analyser may be installed and used at that monitoring station. The decision on the permission for its use rests with the National Competent Authority.

If the site-specific conditions are inside the conditions for which the analyser is type approved, then the uncertainty may be calculated using these site-specific conditions. The evaluations shall be documented.

The analyser shall only be used in the tested configuration.

EN ISO 14956 gives information about typical levels of air pollutants. However, these should be used with proper care for their representativeness for the situations under consideration.

Compounds such as carbon tetrachloride or butanol may be present under site-specific conditions. In such cases, the network operating the analyser should ensure proper determination of benzene by proper choice of separation conditions (analytical column; column temperature program).

9.3 Initial installation

When the analyser and the sampling system have been set up at the monitoring station proper functioning of the analyser and sampling system shall be checked. The results of these checks shall fulfil the requirements and limitations as set out by the manufacturer of the analyser as well as the requirements (such as materials used, residence times and so on) given in this standard. The compliance with the requirements of the manufacturer and requirements set out in this standard shall be documented.

During the initial installation a lack of fit check shall be performed according to 9.6.2.

In addition, the repeatability standard deviation ($s_{r,z}$) at a concentration of 10 % of the annual limit value shall be determined. Eleven successive measurements shall be performed. From the last 10 results of these measurements the repeatability standard deviation ($s_{r,z}$) at a concentration of 10 % of the annual limit value shall be calculated according to Formula (2).

The results shall fulfil the criteria in Table 9.

The repeatability standard deviation shall be combined with the slope of the calibration function to calculate the detection limit of the analyser using Formula (3). The detection limit is used:

- as a criterion for peak rejection;
- when processing data as described in 9.8.

It is permitted that these tests be carried out in the laboratory directly before installation at the site or at installation at the site.

The shortest expected lifetime of a particle filter (6.3.2) at a particular site type shall be tested by measuring the loss of benzene applied to the analyser with and without the filter. The concentration of benzene in the test gas shall be about 10 $\mu g/m^3$. The criterion for replacement is a loss of >3 % of benzene.

The test may be performed at a number of monitoring sites representative of other sites in a network. The results are then generalised for other sites of the same type.

The complete test may be performed before putting the analyser into routine operation. Alternatively, the first test is a part of the initial installation, with following tests performed as a part of routine QA/QC. Consideration should be given to the fact that the latter approach may lead to loss of data that will affect data capture.

NOTE A relatively simple test procedure is the following:

- supply an overflow of test gas to the analyser, passing the filter, using a t-piece;
- measure the concentration of benzene at initial installation;
- after 1 week, again measure the concentration of benzene;
- replace the filter with a new filter and measure the concentration of benzene;
- calculate the loss of benzene from the relative differences in the 2 concentrations;
- repeat the procedure after 2 weeks, 4 weeks, 8 weeks, 16 weeks, etc. until the loss of benzene exceeds the criterion of 3 %;
- establish the maximum lifetime of the filter from the calculated losses.

When the concentrations measured by an analyser at a monitoring station are collected by a data-logger/computer system, then the proper functioning of the data collection shall be checked. When the measured data are transmitted to a central computer system, the transmission process shall be checked as well. Checks shall be performed to an extent ensuring that the actual concentrations measured by the analyser are properly recorded in any data collection system.

Subsequently each time parts of the data registration/transmission process are changed, the proper function of the complete process shall be rechecked.

All checks on the proper function of the data collection/transmission system(s) shall be documented.

9.4 Ongoing quality assurance/quality control

9.4.1 General

Quality control is necessary in order to ensure that the uncertainties of the measured values for benzene in ambient air are kept within the stated limits during extended continuous monitoring periods in the field. This requires that maintenance, test and calibration procedures shall be followed which are essential for obtaining accurate and traceable air quality data. In this section, procedures for maintenance, checks and calibration are given. These procedures are regarded as a minimum necessary for maintaining the required quality level.

The quality of the materials and equipment used in the described test procedures shall be in accordance with the requirements given in this standard and shall not significantly influence the results of these procedures.

If a National Reference Laboratory performs the ongoing quality control procedures, it shall be able to demonstrate that it works in compliance with the requirements of internationally accepted standards for test laboratories.

It is recommended that other competent bodies that perform ongoing quality control procedures work in compliance with the requirements of internationally accepted standards for test laboratories.

NOTE 1 EN ISO/IEC 17025 is a harmonized internationally accepted standard.

NOTE 2 An accreditation by a member body of the European co-operation for Accreditation to EN ISO/IEC 17025 is a demonstration of compliance.

9.4.2 Frequency of calibrations, checks and maintenance

The checks and calibrations together with their frequency are summarized in Table 9. Criteria are also given for readjustment, calibration or maintenance of the analyser.

In applying these criteria the user shall be aware that the combination of a number of performance characteristics being close to their respective action criteria may lead to a violation of the measurement uncertainty data quality objective specified in Annex I of Directive 2008/50/EC (25 % for fixed measurements or 30 % for indicative measurements). The approach to the assessment of measurement uncertainty described in Annex F can be used to check whether such violations occur.

Table 9 — Required frequency of calibration, checks and maintenance

Calibration, checks and maintenance	**Section**	**Frequency**	**Action criteria[c,d]**
Calibration of the analyser	9.5.1	At least every year and after repair	Result at zero > detection limit
Repeatability at 10 % of the level of the annual limit	9.3	At least every year and after repair	0,2 µg/m^3
Repeatability at span of the analyser	9.5.1	In combination with calibration, using the data from the calibration	Repeatability standard deviation at span: 0,25 µg/m^3
Verification of gases used for span checks	9.5.2	At least every year	Span: > 5,0 % from last certified value
Span check	9.6.1	At least every two weeks[a]	Span : ± 5,0 % of initial span value or 0,5 µg/m^3 whichever is greater (when expressed as a concentration)
Lack of fit check (to be performed in laboratory or in field)	9.6.2, Annex A	Within 1 year of the test at initial installation; subsequently: Within 1 year after test if the lack-of-fit is within 2,0 % to 5,0 %; Within 3 years if the lack of fit is ≤ 2,0 %; After repair.	Lack-of-fit > 5 % or 0,5 µg/m3 whichever is greater (when expressed as a concentration) for concentrations > 0 Lack-of-fit > 0,5 µg/m^3 at zero
Testing sample manifold 1) influence of pressure drop induced by the manifold pump 2) sample collection efficiency	 9.6.3.1 9.6.3.2	 At least every three years	 influence ≥ 1 % of measured value or 0,5 µg/m^3 whichever is greater (when expressed as a concentration influence ≥ 2 % of the measured value
Change of particle filter[b]	9.3, 9.7.1	At least every year[b]	Response to test gas passing the filter is ≤ 97 %
Test of the sampling lines	9.7.2	At least every year[b]	≥ 2,0 % sample loss

Calibration, checks and maintenance	Section	Frequency	Action criteria[c,d]
Changing of consumables	9.7.3	As required by manufacturer[b]	As required
Preventive/routine maintenance of components of the analyser	9.7.4	As required by manufacturer	As required

[a] Recommended every 23 h or 25 h.

[b] Dependent on site-specific conditions. Depending on the analyser type and installation, a particle filter may or may not be fitted.

[c] If infringement of an action criterion occurs, corrective actions shall be taken as soon as possible. An evaluation of the influence of the detected infringement on the measurement data produced before the actual correction of the infringement took place shall be given and taken into account during data validation. To ensure that the data capture criterion is met, data will need to be inspected by a trained operator every working day.

[d] The combination of a number of performance characteristics being close to their respective action criteria may lead to a violation of the measurement uncertainty data quality objective specified in Annex I of Directive 2008/50/EC. In this case, the measurement uncertainty shall be re-assessed to ensure conformity with the uncertainty requirements. The approach to the assessment of measurement uncertainty described in Annex F can be used to check when such violations occur.

9.5 Calibration of the analyser

9.5.1 General

Calibration shall be performed at least every year with zero air and at a recommended concentration of around 70 % to 80 % of the certification range, to determine analyser response and drift. Calibrations at higher frequencies will give a better indication of drift and analyser performance.

When the maximum concentrations of benzene measured at a specific site (type) are significantly below the maximum of the certification range of the analyser, e.g. by more than a factor of 10, the concentration at which the calibration is performed may be lowered accordingly. This implies that also the concentrations applied for span checks (9.6.1) and lack of fit tests (9.6.2) should be lowered proportionally.

Calibration gases shall be introduced before the filter. After performing one measurement, 4 successive measurements at span concentration shall be performed to calibrate the analyser. In addition, from these measurements the repeatability standard deviation (s_r) at span level shall be calculated according to Formula (2).

The standard deviation shall comply with the performance criterion in Table 9 at the span level.

Frequency of test:

At least every year and after repair.

Action criteria:

- result of zero air measurement > detection limit;
- span drift beyond the measurement range in use or tolerances set by the user.

Action:

Service the analyser.

If servicing includes manual adjustment to the analyser, this shall only be performed by competent personnel, following strict QA/QC procedures to guarantee documentation and traceability of any adjustment.

After servicing the analyser shall be recalibrated.

9.5.2 Calibration gases

For the calibration of the analyser, several methods are available to generate calibration gases. In Table 3 the various methods are given.

The concentrations of the benzene calibration gases that are used to calibrate the analyser shall be traceable to (inter)nationally accepted standards. Maximum permitted uncertainty in the concentration of gases used for ongoing quality control is 5 % with a level of confidence of 95 %. The gases shall be different from those used for the span checks. However, for each of the methods the user shall demonstrate that the uncertainty of the calibration gas does not add to the uncertainty budget in such a way that data quality uncertainty requirements are exceeded.

The purity of the gases shall be as specified in Table 4. Otherwise, the uncertainty due to the presence of excess impurities shall be included in the uncertainty budget.

9.5.3 Adjustment of analyser readings

After calibration the benzene readings of the analyser as logged by the data acquisition system shall be adjusted in accordance with the following formula:

$$x_{\mathrm{bz}} = (y_{\mathrm{bz}} - x_{\mathrm{bz,zero}}) \times \frac{x_{\mathrm{calgas}}}{x_{\mathrm{bz,cal}} - x_{\mathrm{bz,zero}}} \tag{15}$$

where

x_{bz}	is the corrected benzene reading, in µg/m^3;
x_{calgas}	is the concentration of benzene gas used for calibration of the analyser, in µg/m^3;
$x_{bz,cal}$	is the reading of the analyser during span calibration as logged by the data acquisition system, in µg/m^3;
$x_{bz,zero}$	is the reading of the analyser during the zero calibration as logged by the data acquisition system, in µg/m^3;
y_{bz}	is the reading of the analyser during measurements, in µg/m^3.

9.6 Checks

9.6.1 Span checks

9.6.1.1 Test gases

Test gas can be supplied by gas cylinder, or generated by an external calibrator unit or internally in the analyser. The concentration c_t of the test gas shall be around 70 % to 80 % of either the maximum of the certification range or the user-defined range (see 9.5.1).

The stability of the gases for span checks shall be verified at least every year with use of reference gases traceable to (inter)nationally accepted standards. These gases shall fulfil the specifications in Table 4. The gas used for span checks shall not differ by more than 5 % of the last certified value.

The purity of the benzene gas mixture and zero air used for dilution may be as specified in Table 4. However, it is possible to relax the impurity specifications in the gases for water vapour and organic compounds. In this case the uncertainty due to the presence of excess impurities shall be included in the uncertainty budget where significant.

Action criteria:

Zero : ≤ -0,5 µg/m^3 or ≥ 0,5 µg/m^3

Span : ± 5 % of previous verification or 0,5 μg/m³ whichever is greater (when expressed as a concentration).

Appropriate action:

Service the span or zero gas generation unit.

9.6.1.2 Performance of span checks

Test gas shall be measured for a number of times sufficient to get a stable reading, taking into considering the effect of the measurement time on the data capture.

The test gas should pass through the particle filter, whenever possible.

The differences between two span values obtained from the following formulae shall be calculated to determine if the action criteria have been exceeded:

$$\Delta x_s = \frac{\left| S_i - S_0 \right|}{S_0} \times 100 \tag{16}$$

where

Δx_s is the difference between the readings of the current span check and the span check after calibration in %;

S_i is the reading of the current span check of the analyser;

S_0 is the reading of the most recent span check after calibration of the analyser.

Frequency of test:

At least every two weeks.

Action criteria:

Span drift ± 5 % or 0,5 μg/m³ whichever is greater (when expressed as a concentration).

Appropriate action:

The analyser shall be recalibrated.

9.6.2 Lack of fit

The lack of fit of the analyser shall be tested using at minimum the following concentrations: 0 %, 10 %, 50 % and 90 % of the maximum of the certification range of benzene or the user-defined range (see 9.5.1). At each concentration (including zero) at least 3 measurements shall be performed, the result of the first shall be discarded.

Frequency of test:

- within 1 year of the test at initial installation; subsequently:
  - within 1 year after test if the lack-of-fit is within 2,0 % to 5,0 %;
  - within 3 years if the lack of fit is ≤ 2,0 %;
- after repair.

Action criteria:

> 5,0 % of the measured value or 0,5 μg/m³ whichever is greater (when expressed as a concentration;

> 0,5 μg/m³ for residual at zero.

Appropriate action:

Remove analyser from site for further testing and repair if necessary.

Lack of fit may be checked either in the laboratory or on site.

9.6.3 Testing the sample manifold

9.6.3.1 Procedure for measuring pressure drop induced by the manifold pump

Equipment required: Handheld manometer.

Attach the inlet of manometer to sample port on manifold, leave outlet open to atmospheric pressure; record measured pressure drop.

The resulting pressure drop should be used to calculate the induced effect on the analyser's response using the following formula:

$$\Delta X_{\Delta \mathrm{Pm}} = b_{\mathrm{gp}} \Delta P_{\mathrm{m}} \times 100 \qquad (17)$$

where

$\Delta X_{\Delta Pm}$	is the change in the analyser response due to the influence of the pressure drop induced by the manifold pump in %;
b_{gp}	is the sensitivity coefficient of the analyser to sample gas pressure change expressed as a percentage of the measured value, obtained during the laboratory type approval test;
ΔP_{m}	is the measured pressure drop induced by the manifold pump.

Action criteria:

Influence of the pressure drop induced by the manifold sampling pump on the measured concentration ≤ 1,0 % or 0,5 µg/m^3 whichever is greater (when expressed as a concentration).

Appropriate action:

Reduce flow through manifold to reduce the induced pressure drop so that the criterion is met.

Clean / replace / repair manifold as necessary and re-test.

9.6.3.2 Procedure for testing the sample collection efficiency of the sampling system

The flow rate of the test gas in the sampling system should be such that the residence time is greater than or equal to that found under normal operating conditions. Typical manifold systems (diameter ~30 mm, length 2 m) have a volume of ~1,5 l.

NOTE Individual sampling lines are tested according to 6.3 and 9.6.2.

Frequency of test:

At least every three years

Action criteria:

Sample loss ≥ 2 %.

Appropriate action:

Clean/replace/repair manifold as necessary and re-test.

Possible test procedures for the sample collection efficiency include:

- delivering a test gas containing a known concentration of benzene directly to the manifold and measure the benzene concentrations directly in the test gas and at the end of the manifold;

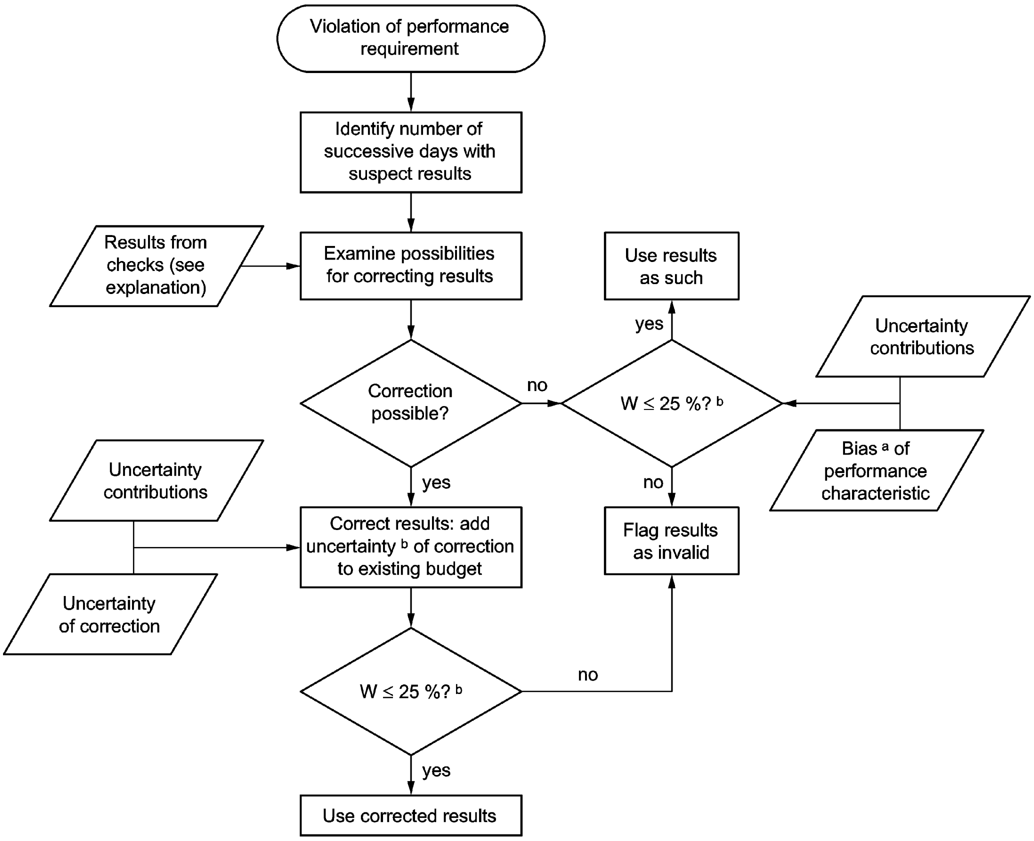
- — add a known flow of a test gas containing a known concentration of benzene to the ambient air sampled and measure the concentrations of benzene at the top and end of the manifold using two separate analysers.

In Annex D an example is given of a possible manifold test performance using the first setup.

9.6.4 Treatment of data after exceedance of performance criteria

If in one of the above checks a violation of a performance criterion has occurred, the effect of this violation on the measurement results obtained between the previous and the current check shall be evaluated. The aim of this evaluation is to attempt to optimize the time coverage and data capture. In principle, the first shall be ≥ 90 % for measurements at industrial sites and ≥ 35 % for other sites; the second shall be ≥ 90 % of measurement time excluding periods of calibration and normal maintenance.

A flow scheme for the performance of this evaluation and for the evaluation of possibilities for correcting data is given below in Figure 3.



[a] The deviation of the value of the performance characteristic from its requirement.

[b] At the level of the annual limit value.

Figure 3 — Flow scheme for performance of evaluation of effects of violation of performance requirements and possibilities for data correction

Checks that would in principle permit application of corrections include:

- — verification of test gases (9.6.1);
- — zero air calibrations (9.5.1);

— span drift checks (9.6.2).

9.7 Maintenance

9.7.1 Change of particle filters

The effective filter lifetime shall be determined as described in (9.3). Filters may be changed at a frequency higher than that determined from the test results, but shall be changed at least every year.

When replacing filters these should be handled wearing gloves or using tweezers.

NOTE The lifetime of the filter will be affected by changes particle composition and/or concentration level and changes in benzene levels at the site (type). As a consequence, the frequency of filter replacement may need to be increased.

New filters shall be conditioned with ambient air for 30 min before any ambient data is considered valid. This conditioning is considered a part of normal maintenance.

Action criteria:

Response to benzene gas mixture passing the filter is ≤ 97 %.

Appropriate action:

Replace the filter.

9.7.2 Change of sampling lines

Sampling lines shall be changed or cleaned at least every year.

9.7.3 Change of consumables as applicable

Generally, the requirements of the manufacturer can be followed. However, at the initial installation the effects of site-specific conditions on consumables lifetime shall be established. Site-specific maintenance periods shall then be devised for the replacement of such consumables.

9.7.4 Preventive/routine maintenance of components of the analyser

The manufacturer’s recommendations should be followed for the routine maintenance of the analyser.

9.8 Data handling and data reports

The competent body responsible for QA/QC of the monitoring station has the responsibility to produce valid data. This implies that the collected data shall be free from data acquired during normal maintenance, faulty data, zero and span checks and calibrations.

Basic values shall have at least one digit more than the number in which the annual limit value for benzene is expressed. For all measurements basic values ≥ –(*detection limit)* shall be accepted for aggregations and calculations. Values < –(*detection limit)* shall be discarded.

When a value that is larger than the maximum of the certification range is reported, this value shall be used in the calculation of averages but these averages shall be flagged in the data report to indicate that this average may have exceeded the uncertainty requirement of Annex I of Directive 2008/50/EC (25 % for fixed measurements or 30 % for indicative measurements).

Rounding of results shall be the last step of any calculation, i.e., immediately before comparing the result with the limit value. For rounding the so-called “commercial rounding” shall be used.

Data collection from the analyser shall be done at a frequency of once per measurement cycle.

Data capture shall be ≥ 75 % of the averaging time.

The response of the analyser to zero or span calibration gases shall be recorded before and after the adjustment of the analyser. Measured drift in the analyser's response that is less than the action criteria in Table 8 may be corrected for in data processing.

9.9 Measurement uncertainty

Annex F describes the assessment of uncertainties of measurement results for annual averaging periods. These assessments are based on combining uncertainty contributions derived from actual values of the performance characteristics obtained from the type-approval tests with practical values obtained as a result of evaluation of QA/QC data, e.g., for zero and span drift, actual ranges of influence characteristics and actual uncertainties of calibration gas mixtures. The assessment does not include the uncertainty contribution of the sampling process. The contribution of data transmission can be neglected in the final uncertainty budget.

The assessment shall be repeated at least every year using actual values of uncertainty contributions estimated from field operation.

NOTE 1 The approach described in Annex F allows the user to compare uncertainty contributions and target QA/QC towards reduction of the largest contributions to uncertainty (see also note under Table 8.

NOTE 2 Other approaches, such as those described in EN ISO 20988 [5], can also be used. These may be particularly useful for analysers for which currently no values of performance characteristics from type-approval tests are available.

10 Expression of results

The readings from the analyser are converted to concentrations using the appropriate conversion factors and the results expressed in micrograms per cubic metre.

The conversion factors at 20 °C and 101,3 kPa are:

1 μg/m^3 benzene = 0,308 nmol/mol benzene

1 nmol/mol benzene = 3,25 μg/m^3 benzene

For conversion at different atmospheric pressures and/or temperatures factors may be derived from the ideal gas law.

11 Test reports and documentation

11.1 Type approval test

The competent body shall prepare a type approval report, which shall contain at least the following information:

a) General:

   1) certification proposal;

   2) unambiguous AMS designation;

   3) measured component(s);

   4) device manufacturer together with full address;

   5) field of application;

   6) measuring range for suitability test;

   7) restrictions: restrictions shall be formulated if testing shows that the analyser does not cover the full scope of possible application fields;

   8) notes: in the event of supplementary or extended testing, reference shall be made to all preceding test reports. Attention shall be drawn to main equipment peculiarities;

   9) test laboratory;

   10) test report number and date of compilation.

b) Task definition:

   1) nature of test: first test or supplementary testing;

   2) objective: specification of which performance criteria were tested; bibliography; scope of any supplementary tests.

c) Description of the analyser tested:

   1) measuring principle: description of metrological and scientific relationships;

   2) analyser scope and set-up: description of all parts of the analyser covered in the scope of testing, if possible including a copy of an illustration or flow diagram showing the analyser; statement of technical specifications, if appropriate in tabular form.

d) Test program: details shall be provided on the test program, in relation to the analyser under test; in the case of supplementary or extended testing, the additional scope of testing shall be detailed and substantiated; particularities of the test shall be documented:

   1) laboratory test: statement of test steps involved;

   2) field test: details on: test steps involved; site type at which the field test examinations were carried out; operating conditions for the analyser under test;

   3) any deviations from test steps and/or conditions prescribed in this European Standard; these shall also be reported on the approval certificate summary page.

e) Test results: comparison of the performance criteria placed on the analyser in the performance test with the results attained. The information below shall be stated for each individual test point in the following order of sequence:

   1) citation of performance criterion;

   2) equipment;

   3) method;

   4) evaluation;

   5) assessment of measurement uncertainty;

   6) detailed presentation of test results allowing for the respective section of the documentation.

The type approval report shall be available to the (potential) user.

11.2 Field operation

11.2.1 Suitability evaluation

The user and/or operator of an analyser or monitoring station shall prepare a report on the suitability evaluation (9.2) of the analyser at the monitoring site. The suitability test report shall contain at least the following information:

a) reference to this European Standard;

b) complete identification of the analyser and monitoring site;

c) results of the suitability evaluation of the analyser at the monitoring site, including the calculated measurement uncertainty;

d) proof of the compliance of the sampling system to this European Standard;

e) checks on the initial installation.

11.2.2 Documentation

The user and/or operator shall document all maintenance, repairs, calibrations, change of calibration units, malfunctionings, etc. for each individual analyser, sampling system and monitoring site, and any deviations from the requirements of this European Standard, provided that these have significant consequences for the quality of the results.

11.2.3 Ambient air quality data reports

Ambient air data reports for benzene shall be prepared according to Chapter V Information and Reporting of Directive 2008/50/EC. The report shall contain at least the following information:

a) reference to this European Standard;

b) percentage of data capture;

c) air quality data presented in the required format;

d) a statement on the measurement uncertainty of the data reported, including:

    1) the type of analyser used;

    2) whether it has been type approved;

    3) a reference to the approach used for uncertainty assessment (e.g. this European Standard).

Annex A
(normative)

Test of lack of fit

A.1 Establishment of the regression line

A linear regression function in the form of $y_i = A + B\,x_i$ is made through calculation of the function:

$$y_\text{i} = a + B\,(x_\text{i} - x_z) \qquad \text{(A.1)}$$

For the regression calculation all measuring points (including zero) are taken into account. The total number of measuring points (n) is equal to the number of concentration levels times the number of repetitions at a particular concentration level.

The coefficient a is obtained from:

$$a = \sum y_i / n \qquad \text{(A.2)}$$

where

a is the average value of the Y-values;

y_i is the individual Y-value;

n is the number of calibration points.

The coefficient B is obtained from:

$$B = \left(\sum y_\text{i}\left(x_\text{i} - x_\text{z}\right)\right) / \sum\left(x_\text{i} - x_\text{z}\right)^2 \qquad \text{(A.3)}$$

where

x_z is the average of the x-values ($= \Sigma\, x_\text{i}/n$);

x_i is the individual x-value.

The function $y_i = a + B\,(x_\text{i} - x_\text{z})$ is converted to $y_i = A + B\,.x_\text{i}$ through the calculation of A:

$$A = a - B\,x_\text{z} \qquad \text{(A.4)}$$

A.2 Calculation of the residuals of the averages

The residuals of the averages of each calibration point (including the zero point) are calculated as follows.

The average of each calibration point (including the zero point) at one and the same concentration c is calculated according to:

$$(y_\text{a})_\text{c} = \sum (y_\text{i})_\text{c} / m \qquad \text{(A.5)}$$

where

$(y_\text{a})_\text{c}$ is the average y-value at concentration level c;

$(y_\text{i})_\text{c}$ is the individual y-value at concentration level c;

m is the number of repetitions at one and the same concentration level c.

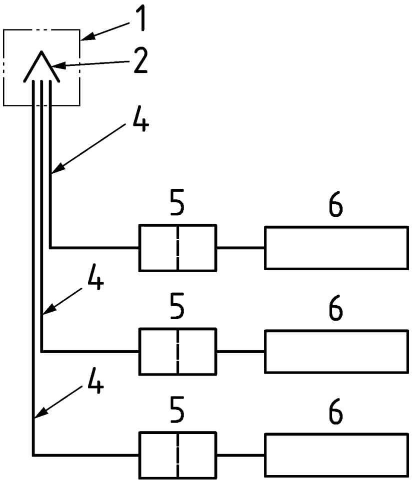
The residual of each average (r_c) at each concentration level is calculated according to:

$$r_c = (y_a)_c - (A + B\,c) \tag{A.6}$$

Each residual to a value relative to its own concentration level c is expressed (in %) as:

$$r_{c,rel} = \frac{r_c}{c} \times 100 \tag{A.7}$$

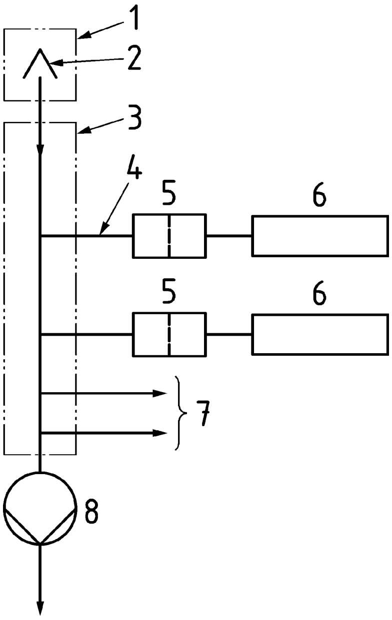
Annex B
(informative)
Sampling equipment



Key

1	sample inlet	5	filter
2	rain shield	6	analyser
4	sampling line		

Figure B.1 — Sampling layout with individual lines



Key

1	sample inlet	5	filter
2	rain shield	6	analyser
3	manifold	7	connection for other analysers or equipment
4	sample line	8	sampling pump for the manifold.

Figure B.2 — Sampling layout with a main sampling manifold

Annex C
(informative)

Components and applications of benzene analysers

Some typical chromatograph systems are listed in Table C.1.

Table C.1 — Typical components of benzene analysers

Monitor	**1**	**2**	**3**	**4**	**5**	**6**
Cycle time min	15	15-30	15-30	15-30	15	60
Sorbents	Carbotrap™/ Carbosieves™ SIII	Tenax™ GR	Carbotrap™/ Carbopack™	Porapak™ SuperQ™	Tenax GR™	Carbotrap™/ Carbosieves™ SIII
Sampling	pump/nozzle	pump/MFC	internal pump	pump/MFC	piston pump	Pump / MFC
Bypass	possible	200 ml		possible	pump	no
Temperature °C	ambient	40	10-35	ambient	ambient	-30
Sample amount	500 ml	300 ml	up to 900/1 800 ml	390 ml	100 ml	800 ml
Carrier gas	H_2	N_2	N_2 or H_2	N_2 or H_2	N_2	He
Desorption:						
Temp. °C	330	230	340	140	180	320
Time	60 s			2,5 min	30 s	60 s
Flow	2 ml/min	11 ml/min	0,5 ml/min			15 ml/min
Injection	350 °C					
Cryo trap	Carbopack™ B					
Stripper column		5 m		CP Sil 5CB. 12 m. 0,53 mm	1,8 m	
Analytical column	1 µm BGB-2.5 (2,5% Phenyl)	Ultimetall 1 µm CP-Wax52CB	EPA 624 type	CP Wax	1,2 µm AT-5	2 columns: Al_2O_3 – Na_2SO_4 (C2-C5), BP1 (C6+)
– **length**	9 m	45 m	10 m	25 m	13 m	60m
– **diameter**	0,2 mm	0,53 mm	0,22 mm	0,53 mm	0,53 mm	0,22mm
Analytical conditions °C	35-180	80	45-140	80	45-60	48-200
Detector	FID	FID	PID or FID	FID	PID 10,6 eV	FID

Monitor	**1**	**2**	**3**	**4**	**5**	**6**
Range	300 µg/m^3	300 µg/m^3	200 µg/m^3	200 µg/m^3	300 µg/m^3	300 µg/m^3
Detection limit	0,16 µg/m^3	0,36 µg/m^3	0,02 µg/m^3 or 0,2 µg/m^3	0,22 µg/m^3	0,2 µg/m^3	<0,1 µg/m^3

Carbosieve™ is a trademark of Sigma Aldrich, USA[1)]

Carbograph™ is a trademark of Alltech Associated, USA[1)]

Carbopack™, is a trademark of Supelco, Inc., USA[1)]

Chromosorb™ is a trademark of Manville Corp, USA[1)]

Porapak™ is a trademark of Waters Associates Inc., USA[1)]

Spherocarb™ is a trade mark of Analabs Inc., USA[1)]

Tenax™ is a trademark of Enka Research Institute, NV, NL[1)]

[1)] This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of the product named. Equivalent products may be used if they can be shown to lead to the same results.

Annex D
(informative)

Manifold testing equipment

Figure D.1 gives the setup for the performance of a manifold test by delivering a test gas containing a known concentration of benzene directly to the manifold and measure the benzene concentrations directly in the test gas and at the end of the manifold. The flow of the test gas should be sufficient to keep its residence time within 6 s.

When the concentration of the benzene delivered is traceable to (inter)nationally accepted standards, only one test needs to be performed using a calibrated analyser. The sample collection efficiency may then be directly calculated as the ratio of the measured and delivered concentrations.

The sample system collection efficiency, E_{ss}, is then calculated as follows:

$$E_{\text{ss}} = \frac{x_{\text{man}}}{x_{\text{ref}}} \times 100 \tag{D.1}$$

where

E_{ss} is the sample system collection efficiency in %;

X_{ref} is reference concentration delivered to the sample manifold;

x_{man} is the mean measured analyser concentration.

When the concentration of the benzene delivered is not traceable, two measurements need to be performed, i.e., one by delivering the benzene gas mixture directly to the analyser, and one in which the mixture is delivered through the manifold. In this case, the correct calibration of the analysers is not necessary, nor is the exact knowledge of the concentration of the test gas. The concentration of the test gas shall be stable.

During testing, the analyser output is collected through the data collection system at the monitoring site under normal site operating procedures.

Data over periods of 5 individual measurements are recorded for each stage of the test. The result of the first measurement shall be discarded, the results of the last 4 measurements shall be averaged.

Sample system collection efficiency, E_{ss}, is then calculated as follows:

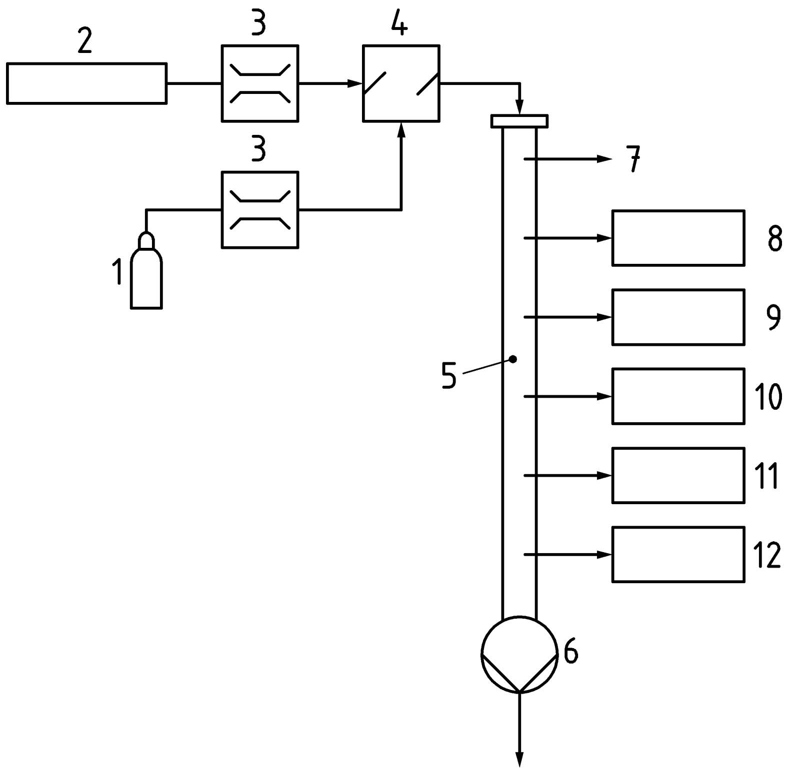
$$E_{\text{ss}} = \frac{x_{\text{man}}}{x_{\text{dir}}} \times 100 \tag{D.2}$$

where

E_{ss} is the sample system collection efficiency in %;

x_{dir} is the mean analyser response to the test gas directly sampled by the analyser;

x_{man} is the mean analyser response to the test gas via the sample manifold.



Key

1	source gas
2	zero-air supply
3	mass-flow controllers
4	mixing chamber
5	sampling manifold
6	sampling pump
7	overflow
8	ozone analyzer
9	carbon monoxide analyzer
10	benzene analyzer
11	sulphur dioxide analyzer
12	nitrogen oxides analyzer

Target concentration benzene is 5 µg/m^3.

Figure D.1 — Schematic Manifold testing equipment

Annex E
(normative)

Type approval

E.1 Type approval and uncertainty calculation

E.1.1 Type approval

The type approval of the analyser consists of the following steps (see 8.6):

a) The value of each individual performance characteristic tested in the laboratory shall fulfil the criterion stated in Table 1 (see 8.3).

b) The expanded uncertainty calculated from the standard uncertainties due to the values of the specific performance characteristics obtained in the laboratory tests shall fulfil the criterion as stated in Annex I of Directive 2008/50/EC (25 % for fixed measurements or 30 % for indicative measurements). This criterion is the maximum uncertainty of individual values of continuous measurements at the annual limit value. The relevant specific performance characteristics and the calculation procedure are given in this annex.

c) The value of each of the individual performance characteristics tested in the field shall fulfil the criterion stated in Table 1 (see 8.2).

d) The expanded uncertainty calculated from the standard uncertainties due to the values of the specific performance characteristics obtained in the laboratory and field tests shall fulfil the criterion as stated in Annex I of Directive 2008/50/EC (25 % for fixed measurements or 30 % for indicative measurements). This criterion is the maximum uncertainty of individual values of continuous measurements at the annual limit value. The relevant specific performance characteristics and the calculation procedure are given in this annex.

The instrument is type approved when all 4 requirements are met.

E.1.2 Uncertainty calculation

For the purpose of application of this standard the combined uncertainty resulting from the laboratory type approval tests is calculated using Formula (E.3).

The combined uncertainty resulting after the additional data from the field tests are available is calculated using Formula (E.19).

E.2 Type approval requirement (a)

Table E.1 gives the performance characteristics that shall be considered in demonstrating compliance with requirement (a) in the type approval procedure and an example of laboratory results.

Table E.1 — Relevant performance characteristics and criteria

No.	Performance characteristic	Symbol	Clause	Performance criterion for benzene [b]	Results lab. test	[c]
1	Repeatability standard deviation at 10% of the level of the annual limit	$s_{r,z}$	8.4.4	≤ 0,20 μg/m^3	0,02	✓
2	Repeatability standard deviation at the level of the annual limit value	$s_{r,ct}$	8.4.4	≤ 0,25 μg/m^3	0,054	✓
3	Lack of fit (residual from the linear regression function)		8.4.5			
3a	Largest residual from the linear regression function at concentrations higher than zero	r_{max}		≤ 5,0 % of the measured value	1,1	✓
3b	Residual at zero	r_z		≤ 0,50 μg/m^3	0,25	✓
4	Sensitivity coefficient of sample gas pressure	b_{gp}	8.4.6	≤ 0,40 μg/m^3/kPa	0,12	✓
5	Sensitivity coefficient of surrounding temperature	b_{st}	8.4.7	≤ 0,08 μg/m^3/K	0,06	✓
6	Sensitivity coefficient of electrical voltage	b_V	8.4.8	≤ 0,08 μg/m^3/V	0,002	✓
7	Interferents at concentration c_t (at a level of the annual limit)		8.4.9			
7a	H_2O with concentration 19 mmol/mol [d]	b_{H2O}		≤ 0,015 μg/m^3/(mmol/mol)	0,010	✓
7b	Organic compound mixture	Δx_{oc}		≤ 0,50 μg/m^3	0,22	✓
8	Carry over (memory effect)	C_m	8.4.10	≤ 1,0 μg/m^3	0,32	✓
11	Short term drift at span level [a]	$D_{l,s}$	8.4.3	≤ 2,0 μg/m^3 over 12 h	0,47	✓
12	Difference sample/calibration port [e]	Δx_{sc}	8.4.11	≤ 1,0 %	0	✓

[a] Span level is around 70 % - 80 % of the certification range.

[b] To demonstrate compliance the absolute value of the performance characteristic shall be taken.

[c] ✓ : requirement is met.

[d] A H_2O-concentration of 19 mmol/mol equals 80 % RH at 20 °C and 101,3 kPa.

[e] If relevant.

CONCLUSION: All values of the performance characteristics obtained in the laboratory tests are complying with the requirements.

Requirement (a) is fulfilled.

E.3 Type approval requirement (b)

E.3.1 General

In type approval requirement (b) the expanded uncertainty calculated from the standard uncertainties due to the values of the specific performance characteristics obtained in the laboratory tests shall fulfil the criterion as stated in Annex I of Directive 2008/50/EC (25 % for fixed measurements or 30 % for indicative measurements). This criterion is the maximum uncertainty of individual values of continuous measurements at the annual limit value.

The model formula for the measurement is based on the assumption that the measured value *c* consists of signal contribution from the concentration of the measurand, c^* and a sum of signal contributions c_K (in units of the measured value) caused by the influence of the considered performance characteristics *k* of the measuring system:

$$c = c^* + \sum_k c_k \tag{E.1}$$

From this model formula the following variance formula is derived which describes the uncertainty of the measured value, *u(c)*, under the conditions of the type approval test:

$$u^2(c) = \sum_k u^2(c_k) \tag{E.2}$$

The values of the following uncertainties shall be included in the calculation of the expanded uncertainty after the laboratory tests.

Table E.2 — Standard uncertainties to be incorporated in the calculation of the expanded uncertainty after the laboratory tests

No.	Standard uncertainty due to	Symbol	Formula
2	Repeatability standard deviation at the annual limit value	u_r	(E.6) – (E.7)
3	Lack of fit at the annual limit value	u_l	(E.8)
4	Variation in sample gas pressure at the annual limit value	u_{gp}	(E.12)
5	Variation in surrounding temperature at the annual limit value	u_{st}	(E.13)
6	Variation in electrical voltage at the annual limit value	u_V	(E.14)
7	Interferences at the annual limit value		
7a	H_2O with concentration 19 mmol/mol	u_{H2O}	(E.15)
8	Carry over (memory effect)	u_m	(E.16)
12	Difference sample/calibration port	$u_{\Delta sc}$	(E.17)

Next to the uncertainties due to these performance characteristics the uncertainty in the concentration of calibration gas and in the calibration itself are incorporated in the uncertainty calculation.

Table E.3 — Standard uncertainty of the calibration gas to be incorporated in the calculation of the expanded uncertainty after the laboratory tests

No.	Standard uncertainty due to	Symbol	Formula
15	Uncertainty in calibration gas	u_{cg}	(E.18)

The calculation of standard uncertainties is based on the procedures laid down in EN ISO 14956.The uncertainty calculation shall be carried out with the values of the performance characteristics at the concentration of the annual limit value (if relevant).

The combined standard uncertainty shall be calculated according to:

$$u_c = \sqrt{u_r{}^2 + u_l{}^2 + u_{gp}{}^2 + u_{st}{}^2 + u_V{}^2 + u_{H_2O}{}^2 + u_m{}^2 + u_{\Delta sc}{}^2 + u_{cg}{}^2} \tag{E.3}$$

where

u_c	is the combined standard uncertainty in µg/m^3;
u_r	is the standard uncertainty for repeatability at level of the annual limit value in µg/m^3;
u_l	is the standard uncertainty for lack of fit at level of the annual limit value in µg/m^3;
u_{gp}	is the standard uncertainty for sample gas pressure variation in µg/m^3;
u_{st}	is the standard uncertainty for surrounding temperature variation in µg/m^3;
u_V	is the standard uncertainty for electrical voltage variation in µg/m^3;
u_{H2O}	is the standard uncertainty for the presence of water vapour in µg/m^3;
u_m	is the standard uncertainty for carry-over (memory effect) in µg/m^3;
$u_{\Delta sc}$	is the standard uncertainty for difference sample/calibration port in µg/m^3;
u_{cg}	is the standard uncertainty for calibration gas in µg/m^3.

The absolute **expanded uncertainty** shall be calculated according to:

$$U = k u_c \qquad \text{(E.4)}$$

with $k = 2$

where

U	is the expanded uncertainty in µg/m^3;
k	is the coverage factor of approximately 95 %;
u_c	is the combined standard uncertainty in µg/m^3;

The relative **expanded uncertainty** shall be calculated according to:

$$W = \frac{U}{l_a} \times 100\% \qquad \text{(E.5)}$$

where

W	is the relative expanded uncertainty in %;
U	is the expanded uncertainty in µg/m^3;
l_a	is the annual limit value of benzene in µg/m^3;

Requirement (b) is fulfilled when: $W \leq W_{\text{req.}}$

E.3.2 Calculation of standard uncertainties

For the calculation of the standard uncertainties the following formulae shall be used.

Repeatability at the annual limit value of benzene

The standard uncertainty for **repeatability at the annual limit value** is calculated according to:

$$u_r = \frac{s_r}{\sqrt{m}} \qquad \text{(E.6)}$$

with

$$s_{\mathrm{r}} = \frac{l_a}{c_{\mathrm{t}}} s_{\mathrm{r,ct}} \tag{E.7}$$

where

u_{r}	is the standard uncertainty for repeatability at the annual limit value in µg/m³;
s_{r}	is the repeatability standard deviation at the annual limit value in µg/m³;
m	is the number of independent measurements performed for obtaining the value of s_{r};
l_a	is the annual limit value in µg/m³;
c_{t}	is the test gas concentration (at the level of the annual limit value) in µg/m³;
$s_{\mathrm{r,ct}}$	is the repeatability standard deviation at the test gas concentration in µg/m³.

Lack of fit

The standard uncertainty due to **lack of fit at the annual limit value** is calculated according to:

$$u_{\mathrm{l}} = \frac{r_{\max}}{100} \frac{l_a}{\sqrt{3}} \tag{E.8}$$

where

u_l	is the standard uncertainty due to lack of fit at the annual limit value in µg/m³;
$r_{\max}$	is the maximum residual from a linear regression function in % calculated according to Annex A;
l_a	is the annual limit value in µg/m³.

Influence quantities

General

The approach taken to quantify the uncertainty contributions due to influence quantities (physical and chemical) is taken directly from EN ISO 14956.

In short: an analyser is calibrated at an influence quantity value q_{cal} and is adjusted before being put into operation.

Subsequently, the analyser is used in the field where ambient values of q may vary between q_{min} and q_{max}. The distribution of the values of q is unknown. The sensitivity coefficient of the variation of response with variations in q has been determined in the type approval test to be b_q µmol/mol/unit.

The maximum positive and negative changes in q are $\Delta q_{max} = q_{max} - q_{cal}$ and $\Delta q_{min} = q_{min} - q_{cal}$

where

q_{max}	is the maximum practical value of the influence quantity;
q_{min}	is the minimum practical value of the influence quantity.

NOTE 1 Δq_{min} is usually negative.

If the distribution of values of q is assumed to be uniform, the uncertainty in the concentration due to the variations in q is

$$u\left(c_q\right)=b_q\sqrt{\frac{\Delta q_{\max}^2+\Delta q_{\max}\Delta q_{\min}+\Delta q_{\min}^2}{3}} \qquad \text{(E.9)}$$

NOTE 2 If a triangular distribution of values of q is appropriate, the denominator value will be 6 instead of 3.

When q_{cal} is unknown, but varies between q_{min} and q_{max}, Formula (E.9) reduces to

$$u\left(c_q\right)=b_q\sqrt{\frac{\left(q_{\max}-q_{\min}\right)^2}{3}} \qquad \text{(E.10)}$$

When q_{cal} is zero, Formula (E.10) reduces to

$$u\left(c_q\right)=b_q\sqrt{\frac{q_{\max}^2+q_{\max}q_{\min}+q_{\min}^2}{3}} \qquad \text{(E.11)}$$

For calculation of uncertainties within the frame of the type-approval test, Formula (E.11) is used.

Sample gas pressure

The standard uncertainty due to variation of **sample gas pressure at the annual limit value** is calculated as:

$$u_{gp}=\frac{l_a}{c_t}b_{gp}\sqrt{\frac{\left(P_2-P_1\right)^2}{3}} \qquad \text{(E.12)}$$

where

u_{gp} is the standard uncertainty due to the influence of pressure in µg/m^3;

b_{gp} is the sensitivity coefficient of sample gas pressure variation in µg/m^3/kPa;

l_a is the annual limit value in µg/m^3;

c_t is the test gas concentration (around 70 % to 80 % of the certification range of benzene) in µg/m^3;

P_1 is the minimum sample gas pressure in kPa;

P_2 is the maximum sample gas pressure in kPa.

Surrounding temperature

The standard uncertainty due to variation of **surrounding temperature at the annual limit value** is calculated as:

$$u_{st}=\frac{l_a}{c_t}b_{st}\sqrt{\frac{\left(T_{S,2}-T_{S,1}\right)^2}{3}} \qquad \text{(E.13)}$$

where

u_{st} is the standard uncertainty due to the variation of the surrounding temperature in µg/m^3;

l_a is the annual limit value in µg/m^3;

c_{t} is the test gas concentration (around 70 % to 80 % of the certification range of benzene) in µg/m^3;

b_{st} is the sensitivity coefficient of the surrounding temperature variation µg/m^3/K;

$T_{\text{S},1}$ is the minimum surrounding temperature in °C;

$T_{S,2}$ is the maximum surrounding temperature in °C.

Electrical voltage

The standard uncertainty due to variation of **electrical voltage at the annual limit value** is calculated as:

$$u_V = \frac{l_a}{c_t} b_V \sqrt{\frac{(V_2 - V_1)^2}{3}} \tag{E.14}$$

where

u_V is the standard uncertainty due to the variation of electrical voltage in µg/m³;

l_a is the annual limit value in µg/m³;

c_t is the test gas concentration (around 70 % to 80 % of the certification range of benzene) in µg/m³;

b_V is the sensitivity coefficient of electrical voltage variation in µg/m³/V;

V_1 is the electrical voltage V_1 in V;

V_2 is the electrical voltage V_2 in V.

Water vapour

The standard uncertainty due to **interference by the presence of water vapour at the annual limit value** is calculated according to:

$$u_{H_2O} = b_{H_2O} \cdot \frac{l_a}{c_t} \sqrt{\frac{c_{H_2O,\max}^2 + c_{H_2O,\max} c_{H_2O,\min} + c_{H_2O,\min}^2}{3}} \tag{E.15}$$

where

$u_{\mathrm{H_2O}}$ is the standard uncertainty due to interference by the presence of water vapour in µg/m³;

$b_{\mathrm{H_2O}}$ is the sensitivity coefficient due to interference by the presence of water vapour in (µg/m³)/(mmol/mol);

c_t is the test concentration of benzene at the level of the annual limit value in µg/m³;

l_a is the annual limit value in µg/m³;

$c_{\mathrm{H_2O,max}}$ is the maximum concentration of water vapour in mmol/mol (= 21 mmol/mol);

$c_{\mathrm{H_2O,min}}$ is the minimum concentration of water vapour in mmol/mol (= 6 mmol/mol).

Carry-over (memory effect)

The standard uncertainty due to **carry over** is calculated according to:

$$u_{\mathrm{m}} = c_m \frac{l_a}{c_t \sqrt{3}} \tag{E.16}$$

where

u_m is the standard uncertainty due to carry over in µg/m^3;

c_m is the effect of carry over in µg/m^3;

c_t is the test concentration of benzene (around 90 % of the maximum of the certification range) in µg/m^3;

l_a is the annual limit value in µg/m^3.

Difference sample/calibration port

The standard uncertainty due to the **difference sample/calibration port** is calculated according to:

$$u_{\Delta sc} = \frac{\Delta x_{sc}}{100} l_a \tag{E.17}$$

where

$u_{\Delta \mathrm{sc}}$ is the standard uncertainty due to the difference sample/calibration port in µg/m^3;

Δx_{sc} is the difference sample/calibration port in %;

l_a is the annual limit value in µg/m^3.

Calibration gas

The standard uncertainty due to the **calibration gas** is calculated according to:

$$u_{\mathrm{cg}} = \frac{W_{cg}}{2 \times 100} l_a \tag{E.18}$$

where

u_cg is the standard uncertainty due to the calibration gas in µg/m^3;

W_cg is the relative expanded uncertainty of the calibration gas in %;

l_a is the annual limit value in µg/m^3.

E.3.3 Example calculation

	benzene annual limit value	5,0		µg/m^3					
								m =	12
Nr	Parameter	C_t		Unit	Value	X-	X+	u	u^2
1	Repeatability at 10% of LV	0,5		µg/m^3	0,20				
2	Repeatability at C_t	5,0		µg/m^3	0,35			0,10	0,02
3	Lack-of-fit			%	1,10			0,03	0,00
4	Sample gas pressure	40		µg/m^3/kPa	0,12	80	110	0,26	0,07
5	Surrounding temperature	40		µg/m^3/K	0,06	273	303	0,13	0,02
6	Electrical voltage	40		µg/m^3/V	0,00	210	240	0,00	0,00
7	Interferents		*Cint*						
7a	- H_2O 19 mmol/mol span	5,0	19	µg/m^3/(mmol/mol)	0,01	6	21	0,01	0,00
7b	- OC mixture	5,0	50	µg/m^3/(µg/m^3)	0,22				
8	Memory effect	40		µg/m^3	0,32			0,02	0,00
9	Field reproducibility			µg/m^3					
10	Long term span drift			%					
11	Short term span drift			µg/m^3	0,35				
12	Difference sample/calibration port			%	0			0	0,00
13	Period of unattended operation			days					
14	Availability			%					
15	Calibration gas			%	3,0			0,08	0,01
	Sum of variances								0,11
	Combined uncertainty (µg/m^3)								0,33
	Expanded uncertainty (%)								13,4%

CONCLUSION W ≤ 25 %. Requirement (b) is met.

E.4 Type approval requirement (c)

Table E.4 gives the performance characteristics that shall be considered in demonstrating compliance with requirement (c) in the type approval procedure.

Table E.4 — Relevant performance characteristics and criteria

No.	Performance characteristic	Symbol	Section	Performance criterion for benzene	Results field test	[b]
9	Reproducibility standard deviation under field conditions	$s_{r,f}$	8.5.5	≤ 0,25 µg/m^3 of the average of a three month period	0,23	✓
10	Long term drift at span level [a]	$D_{l,s}$	8.5.4	≤ 10 % of maximum of certification range	4,8	✓
13	Period of unattended operation		8.5.6	> 14 days or less if manufacturer indicates a shorter period	28	✓
14	Availability of the analyser	A_a	8.5.7	> 90 %	97	✓

[a] Span level is around 70 % - 80 % of the certification range

[b] ✓ : requirement is met

CONCLUSION: All values of the performance characteristics obtained in the field tests are complying with the requirements.

Requirement (c) is fulfilled.

E.5 Type approval requirement (d)

E.5.1 General

In type approval requirement d) the expanded uncertainty calculated from the standard uncertainties due to the values of the specific performance characteristics obtained in the laboratory and field tests shall fulfil the criterion as stated in Annex I of Directive 2008/50/EC (25 % for fixed measurements or 30 % for indicative measurements). This criterion is the maximum uncertainty of continuous measurements at the annual limit value.

The calculation of the expanded uncertainty is based on Formulae (E.1) and (E.2).

The values of the following uncertainties shall be included in the calculation of the expanded uncertainty after the laboratory and field tests:

Table E.5 — Standard uncertainties to be incorporated in the calculation of the expanded uncertainty after the laboratory and field tests

No.	Standard uncertainty due to	Symbol	Formula
2	Repeatability at the annual limit value [a]	u_r	(E.6) – (E.7)
3	Lack of fit at the annual limit value	u_l	(E.8)
4	Variation in sample gas pressure at the annual limit value	u_{gp}	(E.12)
5	Variation in surrounding temperature at the annual limit value	u_{st}	(E.13)
6	Variation in electrical voltage at the annual limit value	u_V	(E.14)
7	Interferents		
7a	H_2O with concentration 19 mmol/mol	u_{H2O}	(E.15)
8	Carry over (memory effect)	u_m	(E.16)
9	Reproducibility under field conditions [a]	$u_{r,f}$	(E.20)
10	Long term drift at the annual limit value	$u_{d,l,la}$	(E.21)
12	Difference sample/calibration port	u_{Dsc}	(E.17)

[a] take for the calculation of the combined standard uncertainty the uncertainty due to the repeatability at the annual limit value or the uncertainty due to the reproducibility under field conditions, whichever is greater

Next to the uncertainties due to these performance characteristics the uncertainty in the concentration of calibration gas and in the calibration itself are incorporated in the uncertainty calculation.

Table E.6 — Standard uncertainty of the calibration gas to be incorporated in the calculation of the expanded uncertainty after the laboratory and field tests

No.	Standard uncertainty due to	Symbol	Formula
15	Uncertainty in calibration gas	u_{cg}	(E.18)

The calculation of standard uncertainties is based on the procedures laid down in EN ISO 14956.The uncertainty calculation shall be carried out with the values of the performance characteristics at the concentration of the annual limit value (if relevant).

Requirement 4 is fulfilled when: $W \leq W_{req}$

The **combined uncertainty** is calculated using the formula:

$$u_c = \sqrt{u_{r,C}^2 + u_l^2 + u_{gp}^2 + u_{st}^2 + u_V^2 + u_{H_2O}^2 + u_m^2 + u_{d,l,la}^2 + u_{\Delta sc}^2 + u_{cg}^2} \qquad (E.19)$$

where

u_c	is the combined uncertainty under field conditions in µg/m³;
$u_{r,C}$	is the highest value of the standard uncertainty for repeatability at the annual limit value and the field reproducibility in µg/m³;
u_l	is the standard uncertainty for lack of fit at the annual limit value in µg/m³;
u_{gp}	is the standard uncertainty for sample gas pressure variation in µg/m³;
u_{st}	is the standard uncertainty for surrounding temperature variation in µg/m³;
u_V	is the standard uncertainty for electrical voltage variation in µg/m³;
u_{H2O}	is the standard uncertainty for the presence of water vapour in µg/m³;
u_m	is the standard uncertainty for carry over in µg/m³;
$u_{d,l,la}$	is the standard uncertainty for long term drift at level of the annual limit value in µg/m³;
$u_{\Delta sc}$	is the standard uncertainty for difference sample/calibration port in µg/m³;
u_{cg}	is the standard uncertainty for calibration gas in µg/m³.

The absolute **expanded uncertainty** shall be calculated according to:

$$U = ku_c \qquad (E.4)$$

with $k = 2$

where

U	is the expanded uncertainty in µg/m³l;
k	is the coverage factor of approximately 95 %;
u_c	is the combined standard uncertainty in µg/m³;

The relative **expanded uncertainty** shall be calculated according to:

$$W = \frac{U}{l_a} \times 100 \qquad (E.5)$$

where

W is the relative expanded uncertainty in %;

U is the expanded uncertainty in µg/m^3;

l_a is the annual limit value in µg/m^3;

E.5.2 Calculation of standard uncertainties

For the calculation of the standard uncertainties the test values as given in E.4 have been used.

The standard uncertainty for **repeatability at the annual limit value** is calculated according to Formulae (E.6) to (E.7).

The standard uncertainty due to **lack of fit at the annual limit value** is calculated according to Formula (E.8).

The standard uncertainty due to variation of **sample gas pressure at the annual limit value** is calculated according to Formula (E.12).

The standard uncertainty due to variation of **surrounding temperature at the annual limit value** is calculated according to Formula (E.13).

The standard uncertainty due to variation of **electrical voltage at the annual limit value** is calculated according to Formula (E.14).

The standard uncertainty due to **interference by the presence of water vapour** is calculated according to Formulae (E.15).

The standard uncertainty due to **carry over** is calculated according to Formula (E.16).

The standard uncertainty due to the **calibration gas** is calculated according to Formula (E.18).

The standard uncertainty due to the **difference sample/calibration port** is calculated according to Formula (E.17).

The standard uncertainty due to the **reproducibility under field conditions at the annual limit value** is calculated according to:

$$u_{r,f} = s_{r,f} \tag{E.20}$$

where

$u_{\mathrm{r,f}}$ is the standard uncertainty due to reproducibility under field conditions in µg/m^3;

$s_{\mathrm{r,f}}$ is the reproducibility standard deviation under field conditions in µg/m^3.

The standard uncertainty due to the **long term drift at level of the annual limit value** is calculated according to:

$$u_{\mathrm{d,l,la}} = \frac{D_{\mathrm{l,s}}}{100} \frac{l_a}{\sqrt{3}} \tag{E.21}$$

where

$u_{\mathrm{d,l,la}}$ is the standard uncertainty due to long term drift at the annual limit value in µg/m^3;

$D_{\mathrm{l,s}}$ is the long term drift at span level in %;

l_a is the annual limit value in µg/m^3.

E.5.3 Example calculation

	benzene annual limit value	5,0		µg/m^3					
								m =	12
Nr	Parameter	C_t		Unit	Value	X-	X+	u	u^2
1	Repeatability at 10 % of LV	0,5		µg/m^3	0,20				
2	Repeatability at C_t	5,0		µg/m^3	0,35			0,10	0,02
3	Lack-of-fit			%	1,1			0,03	0,00
4	Sample gas pressure	40		µg/m^3/kPa	0,12	80	110	0,26	0,07
5	Surrounding temperature	40		µg/m^3/K	0,06	273	303	0,13	0,02
6	Electrical voltage	40		µg/m^3/V	0,002	210	240	0,00	0,00
7	Interferents		*Cint*						
7a	- H_2O 19 mmol/mol span	5,0	19	µg/m^3/(mmol/mol)	0,01	6	21	0,01	0,00
7b	- OC mixture	5,0	50	µg/m^3/(µg/m^3)	0,22				
8	Memory effect	40		µg/m^3	0,32			0,02	0,00
9	Field reproducibility			µg/m^3	0,23			0,23	0,05
10	Long term span drift			%	4,8			0,24	0,06
11	Short term span drift			µg/m^3	0,35				
12	Difference sample/calibration port			%	0			0	0,00
13	Period of unattended operation			days	28				
14	Availability			%	97				
15	Calibration gas			%	3			0,08	0,01
	Sum of variances								0,22
	Combined uncertainty (µg/m^3)								0,47
	Expanded uncertainty (%)								18,9%

CONCLUSION W ≤ 25 %. Requirement (d) is met.

Annex F

(informative)

Calculation of uncertainty in field operation at the annual limit value

F.1 General

This uncertainty evaluation is applied for the suitability evaluation after initial installation of an analyser (9.2) and for the periodic compliance check of the measurement uncertainty (9.9).

F.2 Combined standard uncertainty

In principle, the approach to uncertainty calculation does not differ from that given in E.5. The difference is that here – where possible – practical (actual) values are used for the values of influence quantities.

The **combined standard uncertainty** in an average measurement result at the level of the annual limit value during actual field operation of a measurement system is calculated using the following formula:

$$u_{\mathrm{c,act}} = \sqrt{{u_{\mathrm{r,C}}}^2 + u_l^2 + u_{gp,act}^2 + u_{st,act}^2 + u_{V,act}^2 + u_{H_2O,act}^2 + {u_{\mathrm{m}}}^2 + {u_{\mathrm{d,l,la}}}^2 + \mathrm{u}_{\mathrm{zg}}^2 + {u_{\Delta sc}}^2 + {u_{\mathrm{cg}}}^2} \quad \text{(F.1)}$$

where

$u_{\mathrm{c,act}}$	is the combined uncertainty under actual conditions in µg/m^3;
$u_{\mathrm{r,C}}$	is the highest value of the standard uncertainty for repeatability at the annual limit value and the field reproducibility in µg/m^3;
u_{l}	is the standard uncertainty for actual lack of fit at the annual limit value in µg/m^3;
$u_{\mathrm{gp,act}}$	is the standard uncertainty for actual sample gas pressure variation in µg/m^3;
$u_{\mathrm{gt,act}}$	is the standard uncertainty for actual sample gas temperature variation in µg/m^3;
$u_{\mathrm{st,act}}$	is the standard uncertainty for actual surrounding temperature variation in µg/m^3;
$u_{\mathrm{V,act}}$	is the standard uncertainty for actual electrical voltage variation in µg/m^3;
$u_{\mathrm{H2O,act}}$	is the standard uncertainty for the actual presence of water vapour in µg/m^3;
u_{m}	is the standard uncertainty for carry over in µg/m^3;
$u_{\mathrm{d,l,la}}$	is the standard uncertainty for actual long term drift at level of the annual limit value in µg/m^3;
$u_{\Delta\mathrm{sc}}$	is the standard uncertainty for difference sample/calibration port in µg/m^3;
u_{zg}	is the standard uncertainty of the composition of the zero gas used for calibration in µg/m^3;
u_{cg}	is the standard uncertainty for the calibration gas in µg/m^3.

The absolute **expanded uncertainty** is calculated according to:

$$U = ku_c \quad \text{(F.2)}$$

with $k = 2$

where

U	is the expanded uncertainty in µg/m^3;

k is the coverage factor of approximately 95 %;

u_c is the combined standard uncertainty in µg/m³.

The relative **expanded uncertainty** is calculated according to:

$$W = \frac{U}{l_a} \times 100 \tag{F.3}$$

where

W is the relative expanded uncertainty in %;

U is the expanded uncertainty in µg/m³;

l_a is the annual limit value of benzene in µg/m³.

F.3 Standard uncertainties

The standard uncertainties are calculated with the formulae given in Annex F, using the relevant values of the performance characteristics, the values of the site-specific conditions related to physical and chemical influences, the value of the site-specific conditions related to operational parameters and the actual values of test gas concentrations during the type approval test.

Repeatability at the annual limit value

The standard uncertainty for **repeatability at the annual limit value** is calculated according to:

$$u_r = \frac{s_r}{\sqrt{m \cdot n_a}} \tag{F.4}$$

where

u_r is the standard uncertainty for repeatability at the annual limit value in µg/m³;

s_r is the repeatability standard deviation at the annual limit value in µg/m³ obtained from Formula (E.7)

m is the number of independent measurements performed for obtaining the value of s_r;

n_a is the number of valid measurements in the year used for aggregation.

Lack of fit

The standard uncertainty due to **lack of fit at the annual limit value** is calculated according to Formula (E.8) using actual values for r_{max} obtained from recent linearity tests.

Influence quantities

General

In general, the principal approach described in Annex E applies to the calculation of the uncertainties due to effects of influence quantities (physical and chemical). In short: if the value of the influence quantity q_{cal} at calibration is known and differs from q_{max} or q_{min}, Formula (E.10) applies.

When q_{cal} is unknown, but varies between q_{min} and q_{max}, Formula (E.11) applies. The uncertainty calculations presented here are based on the application of Formula (E.10).

NOTE If it can be demonstrated that a triangular distribution of values of q is appropriate rather than a uniform distribution, the denominator value will be 6 instead of 3.

Sample gas pressure

The standard uncertainty due to variation of **sample gas pressure at the annual limit value** is calculated according to:

$$u_{gp,act} = \frac{l_a}{c_t} b_{gp} \sqrt{\frac{\left(P_{\max} - P_{cal}\right)^2 + \left(P_{\max} - P_{cal}\right)\left(P_{\min} - P_{cal}\right) + \left(P_{\min} - P_{cal}\right)^2}{3}} \tag{F.5}$$

where

$u_{\mathrm{gp,act}}$ is the standard uncertainty due to the influence of actual pressure variations in µg/m^3;

l_a is the annual limit value in µg/m^3;

c_{t} is the test gas concentration (around 70 % to 80 % of the certification range of benzene) in µg/m^3;

b_{gp} is the sensitivity coefficient of sample gas pressure variation in in µg/m^3/kPa;

$P_{\max}$ is the maximum level of the site-specific range of the variation of the sample gas pressure in kPa;

P_{cal} is the sample gas pressure at which the calibration is performed in kPa;

$P_{\min}$ is the minimum level of the site-specific range of the variation of the sample gas pressure in kPa.

When P_{cal} is not known, Formula (F.4) reduces to

$$u_{gp,act} = \frac{l_a}{c_t} b_{gp} \sqrt{\frac{\left(P_{\max} - P_{\min}\right)^2}{3}} \tag{F.5a}$$

Sample gas temperature

The standard uncertainty due to variation of **sample gas temperature at the annual limit value** is calculated according to:

$$u_{gt,act} = \frac{l_a}{c_t} b_{gt} \sqrt{\frac{\left(T_{G,\max} - T_{G,cal}\right)^2 + \left(T_{G,\max} - T_{G,cal}\right)\left(T_{G,\min} - T_{G,cal}\right) + \left(T_{G,\min} - T_{G,cal}\right)^2}{3}} \tag{F.6}$$

where

$u_{\mathrm{gt,act}}$ is the standard uncertainty due to the influence of actual sample gas temperature variations in µg/m^3;

l_a is the annual limit value in µg/m^3

c_{t} is the test gas concentration (around 70 % to 80 % of the certification range of benzene) in µg/m^3;

b_{gt} is the sensitivity coefficient of sample gas temperature variation in µg/m^3/K;

$T_{\mathrm{G,max}}$ is the maximum level of the site-specific range of the variation of the sample gas temperature in °C;

$T_{G,cal}$ is the sample gas temperature at which the calibration is performed in °C;

$T_{\mathrm{G,min}}$ is the minimum level of the site-specific range of the variation of the sample gas temperature in °C.

When $T_{G,cal}$ is not known, Formula (F.5) reduces to

$$u_{gt,act} = \frac{l_a}{c_t} b_{gt} \sqrt{\frac{\left(T_{G,\max} - T_{G,\min}\right)^2}{3}} \tag{F.6a}$$

Surrounding temperature

The standard uncertainty due to variation of **surrounding temperature at the annual limit value** is calculated according to:

$$u_{st,act} = \frac{l_a}{c_t} b_{st} \sqrt{\frac{\left(T_{S,\max} - T_{S,cal}\right)^2 + \left(T_{S,\max} - T_{S,cal}\right)\left(T_{S,\min} - T_{S,cal}\right) + \left(T_{S,\min} - T_{S,cal}\right)^2}{3}} \qquad \text{(F.7)}$$

where

$u_{\mathrm{st,act}}$	is the standard uncertainty due to the influence of actual surrounding temperature variations in µg/m³;
l_a	is the annual limit value in µg/m³;
c_t	is the test gas concentration (around 70 % to 80 % of the certification range of benzene) in µg/m³;
b_st	is the sensitivity coefficient of surrounding temperature variation in µg/m³/K;
$T_{\mathrm{S,max}}$	is the maximum level of the site-specific range of the variation of the surrounding temperature in °C;
$T_{S,cal}$	is the surrounding temperature at which the calibration is performed in °C;
$T_{\mathrm{S,min}}$	is the minimum level of the site-specific range of the variation of the surrounding temperature in °C.

When $T_{S,cal}$ is not known, Formula (F.6) reduces to

$$u_{st,act} = \frac{l_a}{c_t} b_{st} \sqrt{\frac{\left(T_{S,\max} - T_{S,\min}\right)^2}{3}} \qquad \text{(F.7a)}$$

Electrical voltage

The standard uncertainty due to variation of **electrical voltage at the annual limit value** is calculated according to:

$$u_{V,act} = \frac{l_a}{c_t} b_V \sqrt{\frac{\left(V_{\max} - V_{cal}\right)^2 + \left(V_{\max} - V_{cal}\right)\left(V_{\min} - V_{cal}\right) + \left(V_{\min} - V_{cal}\right)^2}{3}} \qquad \text{(F.8)}$$

where

$u_{\mathrm{V,act}}$	is the standard uncertainty due to the influence of actual voltage variations in µg/m³;
l_a	is the annual limit value in µg/m³;
c_t	is the test gas concentration (around 70 % to 80 % of the certification range of benzene) in µg/m³;
b_V	is the sensitivity coefficient of voltage variation in µg/m³/V;
$V_{\max}$	is the maximum level of the site-specific range of the variation of the voltage in V;
V_{cal}	is the voltage at which the calibration is performed in V;
$V_{\min}$	is the minimum level of the site-specific range of the variation of the voltage in V.

When V_{cal} is not known, Formula (F.7) reduces to

$$u_{V,act} = \frac{l_a}{c_t} b_V \sqrt{\frac{\left(V_{\max} - V_{\min}\right)^2}{3}} \tag{F.8a}$$

Interferents

The calculation of the uncertainty due to interferents is based on the actual concentration of the chemical interferents during field operation. Therefore the following formulae have to be used for calculating the uncertainty due to water vapour and other other chemical interferents.

Water vapour

The standard uncertainty due to the actual **presence of water vapour at the annual limit value** is calculated according to:

$$u_{H_2O,act} = b_{H_2O} \sqrt{\frac{c_{H_2O,\max,act}^2 + c_{H_2O,\max,act} c_{H_2O,\min,act} + c_{H_2O,\min,act}^2}{3}} \tag{F.9}$$

where

$u_{\mathrm{H_2O,act}}$	is the standard uncertainty due to actual interference by the presence of water vapour in µg/m^3;
$b_{\mathrm{H_2O}}$	is the sensitivity coefficient due to interference by the presence of water vapour in (µg/m^3)/(mmol/mol);
$c_{\mathrm{H_2O,max,act}}$	is the actual maximum hourly average concentration of water vapour in mmol/mol;
$c_{\mathrm{H_2O,min,act}}$	is the actual minimum hourly average concentration of water vapour in mmol/mol.

Carry over

The standard uncertainty due to **carry over** is calculated according to Formula (E.16).

Reproducibility under field conditions

The standard uncertainty due to the **reproducibility under field conditions** is calculated according to:

$$u_{\mathrm{r,f,la}} = \frac{s_{r,f}}{\sqrt{n_a}} \tag{F.10}$$

where

$u_{\mathrm{r,f,la}}$	is the standard uncertainty at the annual limit value due to reproducibility under field conditions in µg/m^3.
n_{a}	is the number of valid measurements in the year used for aggregation;
$s_{\mathrm{r,f}}$	is the reproducibility standard deviation for benzene from the field test in µg/m^3.

Long term drift at level of the annual limit value

The standard uncertainty due to the **long term span drift at level of the annual limit value** is calculated according to:

$$u_{\mathrm{d,l,la}} = \frac{D_{\mathrm{l,span}}}{100} \frac{l_a}{\sqrt{3}} \tag{F.11}$$

where

$u_{d,l,la}$	is the standard uncertainty due to long term drift at the limit value in µg/m^3;

$D_{\mathrm{l,span}}$	is the long term span drift in %, determined from periodic calibrations over the period of re-assessment of the measurement uncertainty;
l_a	is the annual limit value in µg/m³.

Zero gas

The uncertainty related to the composition of the zero gas used for calibration is calculated from its specifications (Table 4) for benzene as:

$$u_{zg} = \frac{0{,}1}{\sqrt{3}} \text{ in µg/m}^3 \tag{F.12}$$

Calibration gas

The standard uncertainty due to the **calibration gas** is calculated according to Formula (E.18), with the actual uncertainty of the calibration gas.

Difference sample/calibration port

The standard uncertainty due to the **difference sample/calibration port** is calculated according to Formula (E.17).

F.4 Example calculation

	benzene annual limit value	5,0		µg/m^3								
	Number of values for aggregation	100										
	Number of yearly calibrations	1										
Nr	Parameter	C_t		Unit	Value	X-	Xcal	X+	q_{min}	q_{max}	u	u^2
2	Repeatability at C_t	5		µg/m^3	0,35						0,01	
3	Lack-of-fit			%	1,1						0,03	0,00
4	Sample gas pressure	40		µg/m^3/kPa	0,12	97	101	104	-4	7	0,05	0,00
5	Surrounding temperature	40		µg/m^3/K	0,06	273	294	303	-21	9	0,08	0,01
6	Electrical voltage	40		µg/m^3/V	0,00	215	230	240	-15	10	0,00	0,00
7	Interferents		*Cint*									
7a	- H_2O 19 mmol/mol span	5	19	µg/m^3/(mmol/mol)	0,01	6	0	21	6	21	0,14	0,02
8	Memory effect	40		µg/m^3	0,3						0,02	0,00
9	Field reproducibility			µg/m^3	0,23						0,02	0,00
10	Long term span drift			%	4,8						0,24	0,06
11	Short term span drift			µg/m^3	0,4							
12	Difference sample/calibration port			%	0,0						0,00	0,00
13	Period of unattended operation			days	28							
14	Availability			%	97							
15	Calibration gas			%	2,8						0,07	0,00
	Zero gas			µg/m^3	0,06						0,06	0,004
	Sum of variances											0,10
	Combined uncertainty (µmol/mol)											0,31
	Expanded uncertainty (%)											12,5%

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