



BSI Standards Publication

Ambient air — Standard method for the measurement of the concentration of ozone by ultraviolet photometry

National foreword

This British Standard is the UK implementation of EN 14625:2012. It supersedes BS EN 14625:2005 which is withdrawn.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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ISBN 978 0 580 69299 4

ICS 13.040.20

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This British Standard was published under the authority of the Standards Policy and Strategy Committee on 30 September 2012.

Amendments issued since publication

Date	Text affected
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EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 14625

August 2012

ICS 13.040.20

Supersedes EN 14625:2005

English Version

**Ambient air - Standard method for the measurement of the
concentration of ozone by ultraviolet photometry**

Air ambiant - Méthode normalisée de mesurage de la
concentration en ozone par photométrie U.V.

Luftqualität - Messverfahren zur Bestimmung der
Konzentration von Ozon mit Ultraviolett-Photometrie

This European Standard was approved by CEN on 10 May 2012.

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Ref. No. EN 14625:2012: E

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Foreword

This document (EN 14625:2012) 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of an identical text or by endorsement, at the latest by February 2013, and conflicting national standards shall be withdrawn at the latest by February 2013.

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 14625:2005.

The technical changes made since EN 14625:2005 are listed in Annex H of this European Standard.

According to the CEN/CENELEC Internal Regulations, the national standards organisations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, 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 continuous measurement method for the determination of the concentrations of ozone present in ambient air based on the ultraviolet photometric measuring principle. This standard describes the performance characteristics and sets the relevant minimum criteria required to select an appropriate ultraviolet photometric analyser 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 concentration of ozone present in ambient air up to 500 $\mu\text{g}/\text{m}^3$. This concentration range represents the certification range for ozone for the type approval test.

NOTE 1 Other ranges may be used for measurement systems applied at rural locations monitoring ecosystems.

NOTE 2 When the standard is used for other purposes than Directive 2008/50/EC, the ranges and uncertainty requirements may not apply.

The method covers the determination of ambient air concentrations of ozone in zones classified as rural areas, urban and urban-background areas.

The results are expressed in $\mu\text{g}/\text{m}^3$ (at 20 °C and 101,3 kPa).

NOTE 3 500 $\mu\text{g}/\text{m}^3$ of O_3 corresponds to 250 nmol/mol of O_3 at 20 °C and 101,3 kPa.

This standard contains information for different groups of users.

Clauses 5 to 7 and Annexes B and C contain general information about the principles of ozone measurement by ultraviolet photometric analyser and sampling equipment.

Clause 8 and Annex E are specifically directed towards test houses and laboratories that perform type-approval testing of ozone 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 ozone analyser based on the type-approval test results.

Clauses 9 to 11 and Annexes F and G are directed towards monitoring networks performing the practical measurements of ozone 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 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 14956, *Air quality — Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty (ISO 14956)*

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

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

ISO 13964:1998, *Air quality — Determination of ozone in ambient air — Ultraviolet photometric method*

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.

[SOURCE: JCGM 200:2012 (VIM) [2]]

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

3.2 alert threshold

level beyond which there is a risk to human health from brief exposure for the population as a whole and at which immediate steps are to be taken by the Member States

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

3.3 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]]

3.4

analyser

measuring system 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

3.5

availability of the analyser

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

3.6

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.

Note 3 to entry: Often, the first step alone in the above definition is perceived as being calibration.

[SOURCE: JCGM 200:2008 (VIM) [2]]

Note 4 to entry: In the context of this standard, calibration is a comparison of the analyser response to a known gas concentration with a known uncertainty when the information obtained from the comparison is used for the successive adjustment (if needed) of the analyser.

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 co-variances of these other quantities weighted according to how the measurement result varies with changes in these quantities

[SOURCE: ENV 13005:1999]

3.10

coverage factor

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

[SOURCE: ENV 13005:1999]

3.11

designated 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 $3,3 \times (s_z/B)$ where s_z is the standard deviation of analyser response at zero measurand concentration (see 8.4.5) and B is the slope of the calibration function [3].

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 characterised 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: ENV 13005:1999]

Note 3 to entry: For the purpose of this European 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

fall time

difference between the response time (fall) and the lag time (fall)

3.15

independent measurement

individual measurement that is not influenced by a previous individual measurement by separating two individual measurements by at least four response times

Note 1 to entry: The largest value of response time (rise) and response time (fall) are intended.

3.16

individual measurement

measurement averaged over a time period equal to the response time of the analyser

Note 1 to entry: The largest value of response time (rise) and response time (fall) are intended.

Note 2 to entry: This definition differs from the meaning of the concept "individual measurement" in Directive 2008/50/EC [1].

3.17

influence quantity

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

[SOURCE: ENV 13005:1999]

3.18

interferent

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

3.19

lack of fit

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

3.20

lag time

time interval from the moment at which a step change of sample concentration occurs at the inlet of the analyser to the moment at which the output reading reaches a level corresponding to a predefined change of the stable output reading

3.21

long term drift

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

3.22

monitoring station

enclosure located in the field in which an analyser has been installed to monitor concentrations

3.23

parallel measurements

measurements from different analysers, sampling from one and the same sampling manifold, starting at the same time and ending at the same time

3.24

performance characteristic

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

3.25

performance criterion

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

3.26

period of unattended operation

time period over which the drift is within the performance criterion for long term drift

3.27

repeatability (of results of measurement)

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

Note 1 to entry: These conditions are called laboratory repeatability conditions and include:

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

3.28

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:

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

3.29

residence time inside the analyser

time period for the sampled air to be transported from the inlet of the analyser to the UV absorption cell

3.30

residence time in the sampling system

time period for the sampled air to be transferred to the inlet of the analyser

3.31

response time

time interval from the instant at which a step change of sample concentration occurs at the inlet of the analyser to the instant at which the output reading reaches a level corresponding to a predefined change of the output reading

3.32

sampled air

part of ambient air that is transferred through the sampling inlet and sampling system for subsequent measurement

3.33

sample gas temperature

temperature of the sampled gas at the sample inlet

Note 1 to entry: The term 'gas' may refer to a test gas used in type-approval testing or to ambient air transferred to the analyser.

3.34

sampling system

the assembly of components needed to transfer ambient air to the analyser

3.35

short-term drift

difference between zero or span readings at the beginning and end of a 12 h period

3.36

standard uncertainty

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

[SOURCE: ENV 13005:1999]

3.37

surrounding temperature

temperature of the air directly surrounding the analyser

3.38

target value

level fixed with the aim of avoiding, preventing or reducing harmful effects on human health and/or the environment as a whole, to be attained where possible over a given period

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

3.39

total residence time

sum of the residence time in the sampling system and the residence time inside the analyser

3.40

type approval

decision taken by a designated body that the pattern of an analyser conforms to specified requirements

3.41

type approval test

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

3.42

uncertainty (of measurement)

parameter associated with the result of a measurement that characterises the dispersion of the values that could be attributed to the measurand

[SOURCE: ENV 13005:1999]

4 Abbreviated terms

FEP perfluoro-ethylene-propylene;

MFC mass flow controller;

PFA perfluoroalkoxy (polymer resin);

PTFE polytetrafluoroethylene.

5 Principle

5.1 General

This standard describes the method for measurement of the concentrations of ozone in ambient air by means of ultraviolet photometry. The requirements, the specific components of the ultraviolet photometric 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 test 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 15 % for fixed measurements or 30% for indicative measurements, as specified in Directive 2008/50/EC [1]. Requirements and recommendations for quality assurance and quality control are given for the measurements in the field (see 9.4).

5.2 Measuring principle

Sampled air is drawn continuously through an optical absorption cell where it is irradiated by monochromatic radiation, centred on 253,7 nm, from a stabilised low-pressure mercury (Hg) discharge lamp. The UV radiation, which passes through the absorption cell, is measured by a sensitive photodiode or photomultiplier detector and converted to a measurable electrical signal. Absorption of this radiation by the sampled air within the absorption cell is a measure of the ozone concentration in the ambient air.

Two different systems for the measurement of the ultraviolet absorption by ozone are usually employed.

In one system, the ultraviolet absorption by ozone is determined by means of the difference in ultraviolet absorption between a sample cell and a reference cell (dual-cell type).

In the other system, only a single sample cell is employed. The ultraviolet absorption of ozone is determined by alternately supplying sampled air containing ozone to the absorption cell and ozone-free sampled air. Ozone-free sampled air is obtained by passing the sampled air through an ozone catalytic converter in which the ozone is destroyed.

Most modern commercial ozone analysers measure the temperature and pressure of the sampled air in the absorption cell. Using these data, an internal microprocessor automatically calculates the measured ozone concentration relative to some chosen reference conditions. For analysers without this automated pressure and temperature compensation, the concentrations need to be corrected manually to the chosen reference conditions.

The concentration of ozone is measured in volume/volume units (if the analyser is calibrated using a volume/volume standard). The final results for reporting are expressed in $\mu\text{g}/\text{m}^3$ 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, sampling system 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 system. However, the influence of these components on the test results shall be minimised by proper maintenance.

A designated 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 ENV 13005:1999.

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 that the type-approved analyser meets the requirements for all applicable limit values 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

6.1 General

Depending on the installation of the ultraviolet photometric analyser at a monitoring station, a single sampling line for the analyser may be chosen. Alternatively, sampling can take place from a sampling system consisting of 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 minimise 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.

The following factors may, through decrease or increase in the concentration of ozone, contribute to the uncertainty of the measurement when considering the sampling as an integral part of the measurement:

- loss of ozone in the sampling system;

- loss of ozone in the particle filter;
- loss of ozone due to reaction with nitrogen monoxide in the sampling system and in the analyser.

These factors are recognised to be relevant, but currently cannot be quantified for lack of appropriate assessment methods. As a consequence, the contributions of these factors are not considered in the uncertainty assessment applied in this standard. The effect of these factors is minimised through minimum requirements (see 6.3) and application of appropriate QA/QC measures (see 9.4 to 9.6) and maintenance (see 9.7).

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 taken in e.g. a rural area or background area). Guidance and criteria on sampling points on a micro scale are given in Annex III of Directive 2008/50/EC [1].

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 minimise the residence time (see also 6.3.3).

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 B).

The material of the sample inlet as well as the sampling line or manifold can influence the composition of the sample. In practice, the best materials, such as polytetrafluoroethylene (PTFE), perfluoro-ethylene-propylene (FEP), borosilicate glass or stainless steel shall be used. The influence of the material of the sampling inlet and line or manifold on the measured concentrations of ozone due to losses shall be $< 2,0 \%$.

NOTE This value may be achieved when the quality assurance and quality control requirements (see Clause 9) are followed.

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 of the pressure drop along the sampling inlet and line or manifold and the particle filter on the measured concentrations shall be $\leq 1,0 \%$.

6.3.2 Particle filter

A particle filter shall be placed between the sampling line or manifold and the inlet of the analyser. The filter shall retain all particles likely to alter the performance of the analyser. It shall be made of PTFE. The material of the filter housing shall be chemically inert to ozone.

NOTE 1 The filter may be internal to the analyser (see 7.12) or external. In case the analyser contains a built-in filter, an external filter is not necessary.

NOTE 2 A pore size of the filter of $5 \mu\text{m}$ usually fulfils this requirement.

NOTE 3 Suitable materials for the filter housing are for example PTFE, stainless steel, or borosilicate glass.

The particle filter shall be conditioned before used in measurements. 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 six months. Overloading of the filter may cause loss of ozone by reaction with the particle matter and may increase the pressure drop in the sampling line.

6.3.3 Loss of ozone

As NO is generally present in the sampled air, a change in concentration of ozone will occur due to the reaction of NO with O₃ in the sampling inlet and line or manifold, and in the analyser. In practice a significant change in the concentrations of ozone may be avoided when the residence time in the sampling system is ≤ 3 s. The requirement for the residence time in the analyser is ≤ 3 s (see Table 1). Consequently, the total residence time in the sampling system plus analyser shall comply with the performance criterion in Table 1.

Depending on the location of the particle filter, the sampling system can be contaminated by deposition of dust. This can induce losses of ozone. 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 ozone concentrations by sampling ambient air or ozonated 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 hourly and 8-hourly averages.

6.4 Control and regulation of sample flow rate

The sample flow rate into the analyser shall be maintained within the specifications of the manufacturer of the analyser.

NOTE The flow rate into the ultraviolet photometric analyser is usually controlled by means of restrictors.

6.5 Sampling pump for the manifold

When a sampling manifold is used, a pump (or similar device, e.g. a blower) is necessary for sampling ambient air and suction of the ambient air through the sampling manifold. The inlet of the sampling pump for the sampling manifold shall be located at the end of the sampling manifold (see Annex B). 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 and to ensure that the residence time fulfils the requirement given in 6.3.3. To verify the functioning of this pump, it is recommended to install a flow alarm system. An example of a sampling manifold is given in Annex B.

The influence of the pressure drop induced by the manifold sampling pump on the measured concentration shall be $\leq 1,0$ %.

7 Analyser equipment

7.1 General

In Annex C, schematic diagrams are given of two types of ultraviolet photometric ozone analysers.

The ultraviolet photometric analyser consists of the principal components that are described in 7.2 to 7.11.

7.2 Ultraviolet absorption cell

The ultraviolet absorption cell shall be constructed of materials inert to ozone, such as fluorocarbon polymer, borosilicate glass, fused silica or fluorocarbon-coated metal. The cell assembly shall be mechanically stable so that vibration or change in the surrounding temperature does not affect the optical alignment. Provisions shall be available for measuring the temperature and pressure of the gas in the ultraviolet absorption cell.

7.3 Ultraviolet source lamp

The UV lamp (e.g. a low-pressure mercury vapour discharge lamp) shall emit monochromatic UV radiation centred at 253,7 nm. The UV lamp shall be electronically stabilised to ensure a constant UV radiance; any variation in UV radiance during the measurement cycles will result in a measurement bias or noise.

When employing a mercury vapour discharge lamp, the radiation at 185 nm (which photolyses oxygen to produce ozone) shall be eliminated by means of a high-silica glass enclosure or shield.

NOTE Spectral data show that ambient water vapour should not interfere in the UV wavelength region of interest here (about 200 nm to 300 nm). However, it has been observed in some analysers of one manufacturer that the quartz window of the UV source lamp was covered with a significant number of microscopic scratches. This resulted in a measurable variation in light scattering at the internal window surface due to changing humidity in the sample air. Replacement of such faulty windows eliminated this interference.

7.4 UV detector

The optical system shall be designed in such a way that nearly all radiation sensed by the detector is centred at 253,7 nm. The response of this sensor and its associated electronics shall be sufficiently stable so that the analyser meets the required performance criteria.

NOTE Vacuum photodiodes with caesium telluride sensitisation meet this requirement at 253,7 nm and have a negligible sensitivity at other mercury emission wavelengths. Other detectors, such as photomultiplier tubes also satisfy this purpose.

7.5 Ozone-specific scrubber

The ozone-specific scrubber shall contain a material that selectively catalyses the destruction of ozone in the sampled air.

NOTE 1 Manganese dioxide on a metal substrate has been found to do this satisfactorily. Even though this particular compound does not remove any of the other more common pollutant it has been found to partly remove some organic compounds which may be present in the ambient air. Annex A of ISO 13964:1998 lists such interfering chemical compounds.

NOTE 2 A significant decrease in response to ambient ozone may be an indication of scrubber failure. Normally, manufacturers give an average lifetime of such scrubbers; however, the actual lifetime will depend on the sampling location. For example: high pollutant concentrations at an urban-background station may deactivate the scrubber prematurely.

7.6 Switching valve

A switching valve is used to direct the sampled air alternately either through or around the ozone-specific scrubber is required. It shall be made of a material that is inert to ozone, such as a fluorocarbon polymer.

7.7 Temperature indicator

A temperature-measuring device capable of measuring the sampled air in the ultraviolet absorption cell with a repeatability of max 2 K (as expanded uncertainty) is required.

7.8 Pressure indicator

A pressure-measuring device capable of measuring the pressure of the sampled air in the ultraviolet absorption cell with measurement repeatability of 2 kPa (as expanded uncertainty) is required.

7.9 Flow rate indicator

A flow rate indicator shall be included in the analyser. The flow rate shall be measured after passage of the sampled air through the ultraviolet absorption cell.

7.10 Sampling pump for the analyser

The sampling pump is situated at the outlet of the analyser, and draws the sampled air through the analyser. It can be separate or part of the analyser. In any case it shall be capable of operating within the specified flow requirements of the manufacturer of the analyser and pressure conditions required for the UV absorption cell.

7.11 Internal ozone span source

Some analysers are equipped with an internal ozone span source. This ozone span source shall not be used for calibration purposes. The ozone concentrations generated by this internal span source may be used for functional tests only.

7.12 Particle filter

An analyser will generally contain an internal particle filter. This filter shall be considered an integral part of the analyser in type-approval testing.

8 Type approval of ultraviolet photometric ozone analysers

8.1 General

The determination of the concentration of ozone in ambient air shall fulfil the requirement of a maximum uncertainty in the measured values, which is prescribed by Directive 2008/50/EC. In order to achieve an uncertainty less than (or equal to) this required uncertainty, the ultraviolet photometric analyser shall 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 tests 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 ultraviolet photometric analyser meets the criterion of maximum uncertainty prescribed by Directive 2008/50/EC.

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

The type approval procedure shall fulfil the certification requirements laid down in EN 15267-1 and EN 15267-2. A designated body shall perform the type approval tests. The designated body for the type approval test shall be accredited for these activities according to EN ISO/IEC 17025. The type approval shall be awarded by or on behalf of the competent authority.

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:

- a) performance testing of an AMS;
- b) initial assessment of the AMS manufacturer's quality management system;
- c) certification;
- d) post-certification product-surveillance.

EN 15267-2 covers the supplementary requirements for an AMS manufacturer's management system to EN ISO 9001 [6], 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 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 may need to be modified in order to meet the uncertainty criteria in Annex I from Directive 2008/50/EC. 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 designated 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 O ₃
1	Repeatability standard deviation at zero	s_{rz}	8.4.5	x		$\leq 1,0$ nmol/mol
2	Repeatability standard deviation at concentration c_i (at a level of the hourly alert threshold)	$s_{r,ct}$	8.4.5	x		$\leq 3,0$ nmol/mol
3	Lack of fit (residual from the linear regression function)		8.4.6			
3a	Largest residual from the linear regression function at concentrations higher than zero	r_{max}		x		$\leq 4,0$ % of the measured value
3b	Residual at zero	r_z		x		$\leq 5,0$ nmol/mol
4	Sensitivity coefficient of sample gas pressure	b_{gp}	8.4.7	x		$\leq 2,0$ nmol/mol/kPa
5	Sensitivity coefficient of sample gas temperature	b_{gt}	8.4.8	x		$\leq 1,0$ nmol/mol/K
6	Sensitivity coefficient of surrounding temperature	b_{st}	8.4.9	x		$\leq 1,0$ nmol/mol/K
7	Sensitivity coefficient of electrical voltage	b_v	8.4.10	x		$\leq 0,3$ nmol/mol/V
8	Interferents at zero and at concentration c_i (at a level of the hourly alert threshold) ^a		8.4.11			
8a	H ₂ O with concentration 19 mmol/mol ^b	$X_{H_2O,z,ct}$	1)	x		≤ 10 nmol/mol
8b	toluene with concentration 0,5 μ mol/mol	$X_{tol,z,ct}$	2)	x		$\leq 5,0$ nmol/mol

No.	Performance characteristic	Symbol	Section	Lab. test	Field test	Performance criterion for O ₃
8c	m-xylene with concentration 0,5 µmol/mol	$X_{\text{m-xyl,z,ct}}$	3)	x		≤ 5,0 nmol/mol
9	Averaging effect	E_{av}	8.4.12	x		≤ 7,0 % of the measured value
10	Reproducibility standard deviation under field conditions	$s_{r,f}$	8.5.5		x	≤ 5,0 % of the average of a three month period
11	Long-term drift at zero	$D_{l,z}$	8.5.4		x	≤ 5,0 nmol/mol
12	Long-term drift at span level	$D_{l,s}$	8.5.4		x	≤ 5,0 % of maximum of certification range
13	Short-term drift at zero	$D_{s,z}$	8.4.4	x		≤ 2,0 nmol/mol over 12 h
14	Short-term drift at span level	$D_{s,s}$	8.4.4	x		≤ 6,0 nmol/mol over 12 h
15	Response time (rise)	t_r	8.4.3	x		≤ 180 S
16	Response time (fall)	t_f	8.4.3	x		≤ 180 S
17	Difference between rise time and fall time	t_d	8.4.3	x		≤ 10 S
18	Difference between sample/calibration port ^c	ΔX_{sc}	8.4.13	x		≤ 1,0 %
19	Period of unattended operation		8.5.6		x	3,0 months or less if manufacturer indicates a shorter period
20	Availability of the analyser	A_a	8.5.7		x	> 90 %
21	Residence time in the analyser		8.4.14			≤ 3,0 S
^a Performance criterion is set both at zero and span level. ^b A H ₂ O-concentration of 19 mmol/mol equals 80 %RH at 20 °C and 101,3 kPa. ^c If relevant.						
NOTE nmol/mol = ppb						

8.3 Design change

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 as follows:

- 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. The manufacturer shall evaluate all changes to a type-approved analyser. Where Type 2 changes are identified, further evaluation shall be carried out by a test laboratory in liaison with the relevant body. It is essential that the manufacturer documents all changes and evaluations in accordance with the requirements of EN ISO 9001 and EN 15267-2 in such a way that they can be audited.

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.

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

8.4.1 General

A designated 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 standard. The tests shall be performed on at least two analysers in the laboratory test.

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 auto rescaling and self-correction for drift are optional to the analyser, then these functions shall be disabled during the laboratory tests.

If an auto-rescaling function or self-correction function are not optional and considered a "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.

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

Most analyser systems are able to give an output signal as a moving average over an adjustable period of time and some systems automatically change this integration time as a function of the frequency of the fluctuations in concentration of the detected pollutant. These options are typically used in order to smooth output data. It needs no demonstration that the set value for the averaging time or the use of an active filter will influence the result of the averaging test and response time test. During laboratory and field tests for the type approval, the settings of the monitor shall be as the manufacturer requires. Auto zeroing and auto-scaling capabilities shall be disabled during the lab tests; during field tests the monitor shall be in the configuration as used. All settings shall be noted 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 in, see 8.4.7)	$\pm 0,2$ kPa
Sample gas temperature	20 °C to 23 °C (except for the sample gas temperature test, see 8.4.8)	± 2 °C
Surrounding temperature	20 °C to 23 °C (except for the temperature of the surrounding air test, see 8.4.9)	± 2 °C
Electrical voltage ^a	At nominal line voltage and within manufacturer's specifications (except for the voltage dependence test, see 8.4.10)	± 1 %
Sample flow to the analyser	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 European 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
Generation of an ozone calibration gas	Preparation by means of an ozone generator	ISO 13964:1998, 5.2 point b
Generation of an ozone calibration gas	Dynamic dilution of ozone-air mixtures	EN ISO 6145-6 or EN ISO 6145-7
Calibration	Using a primary UV reference photometer ^a	ISO 13964:1998, 6.2/6.2.1/6.2.2 and 7/7.1
Calibration	Using gas-phase titration with NO	ISO 15337
^a The uncertainty of the readings of the reference photometer includes the uncertainty of the absorption cross section.		

NOTE Guidance to the correct application of gas-phase titration can be found in VDI 2453-2 [4] and ISO 15337 [7].

The maximum permitted expanded uncertainties (95 % confidence) in the concentration of gases used for laboratory tests: 3 %. Possible contamination of zero and span gas shall not significantly influence the results of the laboratory tests. Therefore the span gases and zero gas shall meet the specifications given in Table 4.

Table 4 — Specification for purity of zero air and the air feeding the ozone generator

Pollutant	Concentration
Ozone	≤ 1 nmol/mol
Xylenes	≤ 1 nmol/mol
Toluene	≤ 1 nmol/mol
Water	≤ 150 μ mol/mol

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

8.4.3 Response time

8.4.3.1 General requirements

The response time of the analyser shall be determined at the nominal sample flow rate specified by the manufacturer.

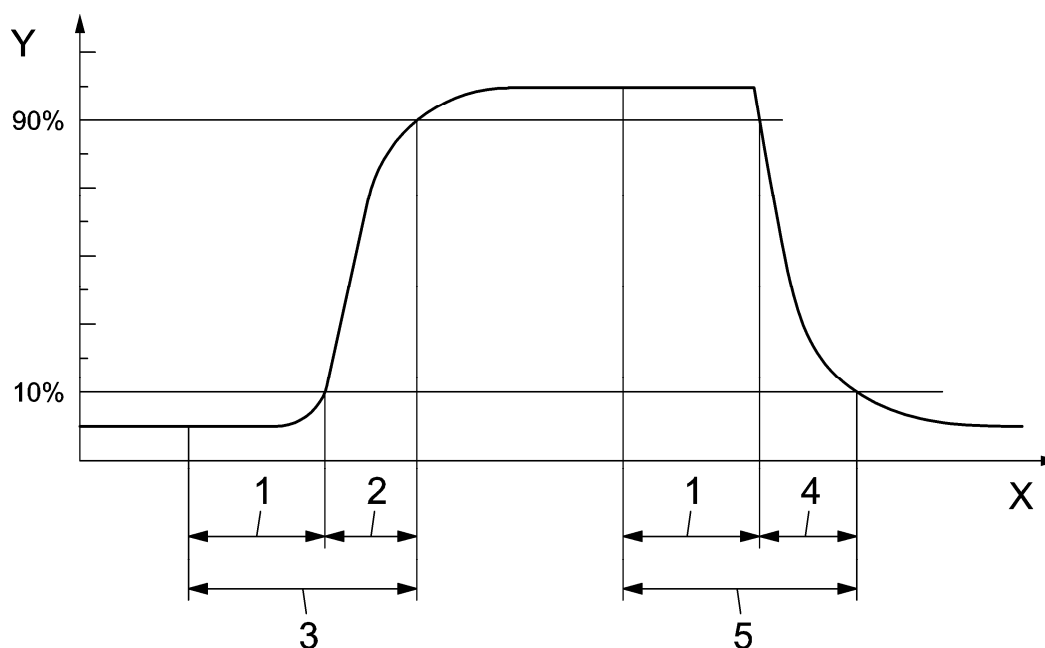
The sample flow rate shall be kept constant within the requirements as given in 8.4.2 (± 1 %) during the test.

8.4.3.2 Test procedure

The determination of the response time shall be carried out by applying to the analyser a step function in the concentration from less than 20 % to about 80 % of the maximum of the certification range of ozone and vice versa (see Figure 1).

NOTE Usually zero gas and span gas are used for this test.

The change from zero gas to span gas and vice versa needs to be made almost instantaneously, with the use of a suitable valve. The valve outlet shall be mounted direct to the inlet of the analyser, and both zero gas and span gas shall have the same amount of gas in excess, which is vented by the use of a tee. The gas flows of both zero gas and span gas shall be chosen in such a way that the dead time in the valve and tee can be neglected compared to the lag time of the analyser system. The step change is made by switching the valve from zero gas to span gas. This event needs to be timed and is the start ($t = 0$) of the (rise) lag time according to Figure 1. When the reading over 5 min is constant to within ± 2 % of the test gas (span) concentration, the span gas can be changed to zero gas again; this event is the start ($t = 0$) of the (fall) lag time. When the reading over 5 min is stable to within 3 nmol/mol of the zero gas concentration the whole cycle as shown in Figure 1 is complete.



Key

- Y analyser response
- X time
- 1 lag time
- 2 rise time
- 3 response time (rise)
- 4 fall time
- 5 response time (fall)

Figure 1 — Diagram illustrating the response time

The elapsed time (response time) between the start of the step change and reaching 90 % of the analyser final stable reading of the applied concentration shall be measured. The whole cycle shall be repeated four times. The average of the four response times (rise) and the average of the four response times (fall) shall be calculated.

The difference in response times shall be calculated according to:

$$t_d = \bar{t}_r - \bar{t}_f \quad (1)$$

where

t_d is the difference between response time (rise) and response time (fall), in s;

$\bar{t}_r$ is the response time (rise) (average of the four response times - rise), in s;

$\bar{t}_f$ is the response time (fall) (average of the four response times - fall), in s.

t_d , $\bar{t}_r$ and $\bar{t}_f$ shall comply with the performance criteria in Table 1.

8.4.4 Short-term drift

After the required stabilisation period (8.4.2.1), the analyser shall be adjusted at zero and span level (around 70 % to 80 % of the maximum of the certification range of ozone). Wait the time equivalent to one independent reading and then record 20 individual measurements, first at zero and then at span concentration. From these 20 measurements, the average is calculated for zero and span level.

The analyser shall be kept running under the laboratory conditions (8.4.2.2) while analysing ambient air. After a period of 12 h, zero and span gas is fed to the analyser. Wait the time equivalent to one independent reading and then record 20 individual measurements, first at zero and then at span concentration. The averages for zero and span level shall be calculated.

NOTE Compliance with this test shows that drift is not the dominant factor in any of the test results.

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

$$D_{s,z} = (C_{z,2} - C_{z,1}) \quad (2)$$

where

$D_{s,z}$ is the 12-hour drift at zero, in nmol/mol;

$C_{z,1}$ is the average concentration of the measurements at zero at the beginning of the drift period, in nmol/mol;

$C_{z,2}$ is the average concentration of the measurements at zero at the end of the drift period, in nmol/mol.

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

$$D_{s,s} = (C_{s,2} - C_{s,1}) - D_{s,z} \quad (3)$$

where

$D_{s,s}$ is the 12-hour drift at span, in nmol/mol;

$C_{s,1}$ is the average concentration of the measurements at span level at the beginning of the drift period, in nmol/mol;

$C_{s,2}$ is the average concentration of the measurements at span level at the end of the drift period, in nmol/mol.

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

8.4.5 Repeatability standard deviation

After waiting the time equivalent of one independent reading 20, individual measurements both at zero concentration and at a test concentration (c_t) similar to the hourly alert threshold value shall be performed.

From these measurements, the repeatability standard deviation (s_r) at zero concentration and at concentration c_t (hourly alert threshold value) shall be calculated according to:

$$s_r = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}} \quad (4)$$

where

s_r is the repeatability standard deviation, in nmol/mol;

x_i is the i th measurement, in nmol/mol;

$\bar{x}$ is the average of the 20 measurements, in nmol/mol;

n is the number of measurements, $n = 20$.

The repeatability standard deviation shall be calculated separately for both series of measurements (zero gas and concentration c_t).

s_r shall comply with the performance criterion in Table 1, both at zero and at the test concentration c_t (hourly alert threshold value).

The repeatability standard deviation at zero is used in combination with the slope of the calibration function determined in 8.4.6 to calculate the detection limit of the analyser as [3]:

$$l_{\text{det}} = 3,3 \cdot \frac{s_{r,z}}{B} \quad (5)$$

where

l_{det} is the detection limit of the analyser, in nmol/mol;

$s_{r,z}$ is the repeatability standard deviation at zero, in nmol/mol;

B is the slope of the calibration function determined according to Annex A using the data from 8.4.6.

8.4.6 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 95 % of the maximum of the certification range of ozone, using at least six concentrations (including the zero point). The analyser shall be adjusted at a concentration of about 80 % of the maximum of the certification range. At each concentration (including zero) at least five individual measurements shall be performed.

The concentrations shall be applied in the following sequence: 80 %, 40 %, 0 %, 60 %, 20 % and 95 %. After each change in concentration, at least four response times shall be taken into account before the next measurement is performed.

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 1. The value of the relative residual value at the level of the hourly alert threshold value shall be taken in the calculation of type approval requirements 2 and 4.

8.4.7 Sensitivity coefficient to sample gas pressure

Measurements are taken at a concentration of about 70 % to 80 % of the maximum of the certification range of ozone at an absolute pressure of about $(80 \pm 0,2)$ kPa and at an absolute pressure of about $(110 \pm 0,2)$ kPa. At each pressure after waiting the time equivalent to one independent reading, three individual measurements are recorded. From these three measurements, the averages at each pressure are calculated.

Measurements at different pressures shall be separated by at least four response times.

The sample gas pressure influence is calculated by:

$$b_{gp} = \left| \frac{(C_{P2} - C_{P1})}{(P_2 - P_1)} \right| \quad (6)$$

where

b_{gp} is the sample gas pressure sensitivity coefficient, in nmol/mol/kPa;

C_{P1} is the average concentration of the measurements at sampling gas pressure P_1 , in nmol/mol;

C_{P2} is the average concentration of the measurements at sampling gas pressure P_2 , in nmol/mol;

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.

8.4.8 Sensitivity coefficient to sample gas temperature

Measurements shall be performed at sample gas temperatures of $T_{G,1} = 0\text{ °C}$ and $T_{G,2} = 30\text{ °C}$. A concentration around 70 % to 80 % of the maximum of the certification range of ozone shall be applied. Wait the time equivalent to one independent and record three individual measurements at each temperature. The sample gas temperature, measured at the inlet of the analyser, shall be held constant for at least 30 min.

The influence of sample gas temperature is calculated from:

$$b_{gt} = \left| \frac{(C_{GT,2} - C_{GT,1})}{(T_{G,2} - T_{G,1})} \right| \quad (7)$$

where

b_{gt} is the sample gas temperature sensitivity coefficient, in nmol/mol/°C;

$C_{GT,1}$ is the average concentration of the measurements at sample gas temperature $T_{G,1}$, in nmol/mol;

$C_{GT,2}$ is the average concentration of the measurements at sample gas temperature $T_{G,2}$, in nmol/mol;

$T_{G,1}$ is the minimum sample gas temperature, in °C;

$T_{G,2}$ is the maximum sample gas temperature, in °C.

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

8.4.9 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 (within the specifications of the manufacturer):

- 1) at the minimum temperature $T_{S,1} = 0\text{ °C}$;
- 2) at the temperature $T_{S,0}$: see Table 2;
- 3) at the maximum temperature $T_{S,2} = 30\text{ °C}$;

For these tests, a climate chamber is necessary.

A concentration around 70 % to 80 % of the maximum of the certification range of ozone shall be applied. At each temperature setting after waiting the time equivalent to one independent reading three individual measurements at zero and at span shall be recorded.

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

The sequence of test temperatures is as follows: $T_{S,0}$, $T_{S,1}$, $T_{S,0}$ and $T_{S,0}$, $T_{S,2}$, $T_{S,0}$

At the first temperature ($T_{S,0}$) the analyser shall be adjusted at zero and at span level (70 % to 80 % of the maximum of the certification range). Then three individual measurements are recorded after waiting the time equivalent to one independent reading at $T_{S,0}$, at $T_{S,1}$ and again at $T_{S,0}$. This measurement procedure shall be repeated at the temperature sequence of $T_{S,0}$, $T_{S,2}$, and at $T_{S,0}$.

In order to exclude any possible drift due to factors other than temperature, the measurements at $T_{S,0}$ are averaged, which is taken into account in the following formula for calculation of the sensitivity coefficient for temperature dependence:

$$b_{st} = \left| \frac{x_T - \frac{x_1 + x_2}{2}}{T_S - \overline{T_{S,0}}} \right| \quad (8)$$

where

b_{st} is the surrounding temperature sensitivity coefficient at zero or span and at $T_{S,1}$ or $T_{S,2}$, in nmol/mol/°C;

x_T is the average of the measurements at $T_{S,1}$ or $T_{S,2}$, in nmol/mol;

x_1 is the first average of the measurements at $T_{S,0}$, in nmol/mol;

x_2 is the second average of the measurements at $T_{S,0}$, in nmol/mol;

T_S is the extreme surrounding temperature at which the test is performed, in °C;

$\overline{T_{S,0}}$ is the average of the surrounding temperatures at set point (see Table 2), in °C;

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

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

For reporting the surrounding temperature dependence the higher value is taken of the two calculations of the temperature dependence at $T_{S,1}$ and $T_{S,2}$.

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

8.4.10 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 zero concentration and at a concentration around 70 % to 80 % of the maximum of the certification range of ozone. After waiting the time equivalent to one independent reading, three individual measurements at each voltage and concentration level shall be recorded.

The voltage dependence is calculated from:

$$b_v = \left| \frac{(C_{V_2} - C_{V_1})}{(V_2 - V_1)} \right| \quad (9)$$

where

- b_v is the voltage sensitivity coefficient, in nmol/mol/V;
- C_{V_1} is the average concentration reading of the measurements at voltage V_1 , in nmol/mol;
- C_{V_2} is the average concentration reading of the measurements at voltage V_2 , in nmol/mol;
- V_1 is the minimum voltage in V specified by the manufacturer;
- V_2 is the maximum voltage in V specified by the manufacturer.

For reporting the dependence on voltage, the highest value of the result at zero and span level shall be taken.

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 over the range of $\pm 10\%$ of the nominal voltage.

8.4.11 Interferents

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 zero and at a test concentration (c_t) similar to the hourly alert threshold value.

The concentration of the mixtures of the test gases with the interferent shall have an expanded uncertainty of $\leq 5\%$ and shall be traceable to (inter)nationally accepted standards. The interferents to be tested and their respective concentrations are given in Table 1. The influence of each interferent shall be determined separately. 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 zero and span level, the analyser shall be fed with a mixture of zero gas and the interferent to be investigated with the concentration as given in Table 1. With this mixture, one independent measurement followed by two individual measurements shall be carried out. This procedure shall be repeated with a mixture of the measurand at concentration c_t and the interferent to be investigated. The influence quantity at zero and concentration c_t are calculated from:

$$X_{\text{int},z} = x_z \quad (10)$$

$$X_{\text{int},c_t} = x_{c_t} - c_t \quad (11)$$

where

- $X_{\text{int},z}$ is the influence quantity of the interferent at zero, in nmol/mol;
- x_z is the average of the measurements at zero, in nmol/mol;
- X_{int,c_t} is the influence quantity of the interferent at concentration c_t , in nmol/mol;
- x_{c_t} is the average of the measurements at concentration c_t , in nmol/mol;
- c_t is the concentration of the applied gas at the level of the hourly alert threshold value, in nmol/mol.

The influence quantities of the interferents shall comply with the performance criteria in Table 1, both at zero and at concentration c_t .

8.4.12 Averaging test

The averaging test gives a measure of the uncertainty in the averaged values caused by short-term concentration variations in the sampled air shorter than the time scale of the measurement process in the analyser. In general, the output of an analyser is a result of the determination of a reference concentration (normally zero) and the actual concentration which takes a certain time.

For the determination of the uncertainty due to the averaging, the following concentrations are applied to the analyser and readings are taken at each concentration (see Figure 2): a stepwise varied concentration of O₃ between zero and concentration c_t similar to the hourly alert threshold value.

The time period (t_c) of the constant O₃ concentration shall be at least equal to a period necessary to obtain four independent readings (which is equal to at least 16 response times). The time period (t_v) of the varying O₃ concentration shall be at least equal to a period to obtain four independent readings. The time period (t_{O_3}) for the O₃ concentration shall be 45 s followed by a period (t_{zero}) of 45 s of zero concentration.

Further:

c_t is the test gas concentration, in nmol/mol;

t_v is a time period including a whole number of t_{O_3} and t_{zero} pairs, and contains a minimum of three such pairs, in s.

The change from t_{O_3} to t_{zero} shall be within 0,5 s. The change from t_c to t_v shall be within one response time of the analyser under test.

The averaging effect (E_{av}) is calculated according to:

$$E_{av} = \frac{C_{av,c} - 2C_{av,v}}{C_{av,c}} \times 100 \quad (12)$$

where

E_{av} is the averaging effect, in %;

$C_{av,c}$ is the average of the at least four independent measurements during the constant concentration period (t_c), in nmol/mol;

$C_{av,v}$ is the average of the at least four independent measurements during the variable concentration period (t_v), in nmol/mol.

The test sequence shall be repeated at least three times. The average of the results for E_{av} shall be reported.