SLOVENSKI STANDARD

SIST EN 14625:2012

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Zunanji zrak - Standardna metoda za določevanje koncentracije ozona z ultravijolično fotometrijo

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

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

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

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English Version

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

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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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Contents

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of an identical text or by endorsement, at the latest by February 2013, and conflicting national standards shall be withdrawn at the latest by February 2013.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.

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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 μg/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 μg/m^3 (at 20 °C and 101,3 kPa).

NOTE 3 500 μg/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 x (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 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, 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 ≤ 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 µm usually fulfils this requirement.