



# SLOVENSKI STANDARD

## SIST EN 14625:2005

01-september-2005

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Učinki okoljskega zrakovega onesnetja zaradi ozona v okoljski zrakovi kakovosti - Standardna metoda za merjenje koncentracije ozona s ultravijolično fotometrijo

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

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

Qualité de l'air ambiant - Méthode normalisée pour le mesurage de la concentration en ozone par photométrie U.V.

**Ta slovenski standard je istoveten z: EN 14625:2005**

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EUROPEAN STANDARD

EN 14625

NORME EUROPÉENNE

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ICS 13.040.20

English version

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

Qualité de l'air ambiant - Méthode normalisée de mesurage de la concentration d'ozone par photométrie UV

Luftqualität - Messverfahren zur Bestimmung von Ozon in Luft mit dem UV-Verfahren

This European Standard was approved by CEN on 10 December 2004.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

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

Management Centre: rue de Stassart, 36 B-1050 Brussels

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## Foreword

This document (EN 14625:2005) has been prepared by Technical Committee CEN/TC 264 "Air quality", the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by September 2005, and conflicting national standards shall be withdrawn at the latest by September 2005.

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

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## 1 Scope

This document specifies a continuous measurement method for the determination of the concentration of ozone present in ambient air based on the ultraviolet photometric measuring principle. This document describes the performance characteristics, and sets the relevant minimum criteria required to select an appropriate ultraviolet photometric ozone 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 Directives data quality requirements and requirements during sampling, calibration and quality assurance.

The method is applicable to the determination of the mass concentration of ozone present in ambient air in the range from  $0 \mu\text{g}/\text{m}^3$  to  $500 \mu\text{g}/\text{m}^3$ . This concentration range represents the certification range for the type approval test.

NOTE 1  $0 \mu\text{g}/\text{m}^3$  to  $500 \mu\text{g}/\text{m}^3$  of  $\text{O}_3$  corresponds to 0 nmol/mol to 250 nmol/mol of  $\text{O}_3$ .

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

NOTE 2 Other ranges may be used for measurement systems applied at rural locations monitoring Ecosystems.

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

When the standard is used for other purposes than the EU-directive, the range and uncertainty requirements need not apply.

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## 2 Normative references

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

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

EN ISO 14956:2002, *Air quality — Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty (ISO 14956:2002)*

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

## 3 Terms and definitions

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

### 3.1

#### **ambient air**

outdoor air in the troposphere excluding workplace air<sup>1</sup>

### 3.2

#### **sample gas temperature**

temperature at the sampling inlet outside the monitoring station

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<sup>1</sup>) As stated in the relevant EU-legislation.

**EN 14625:2005 (E)****3.3****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

**3.4****calibration**

comparison of the analyser response to a known gas concentration with a known uncertainty

**3.5****certification range**

concentration range for which the analyser is type approved

**3.6****combined standard uncertainty**

calculation result of combining the uncertainties determined from all performance characteristics specified in this document according to the prescribed procedures given in this document

**3.7****coverage factor**

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

**3.8****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

NOTE It is recommended that the designated body is accredited for the specific task according to EN ISO 17025.

**3.9****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 for the purpose of this document 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 %

**3.10****fall time**

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

**3.11****independent measurement**

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

**3.12****individual measurement**

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

**3.13****influence quantity**

quantity that is not the measurand but that affects the result of the measurement (VIM 2.7), either an interferent influence quantity (i.e. the concentration of a substance in the air under investigation that is not the measurand), or an external influence quantity (i.e. a quantity that is not the measurand nor the concentration of a substance in the air mass under investigation)

NOTE Examples are:

- presence of interfering gases in the flue gas matrix (interferent influence quantity);
- temperature of the surrounding air (external influence quantity);



- atmospheric pressure (external influence quantity);
- pressure of the gas sample (external influence quantity).

**3.14****interference**

response of the analyser to interferents

**3.15****interferent**

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

**3.16****initial ozone concentration**

ozone concentration in the ambient air just before entrance into the sampling inlet

**3.17****lag 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 10 % of the stable output reading

**3.18****lag time (fall)**

lag time for a negative step change

**3.19****lag time (rise)**

lag time for a positive step change

**3.20****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

**3.21****lack of fit**

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

**3.22****long-term drift**

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

**3.23****monitoring station**

enclosure located in the field in which an ozone analyser has been installed in such a way that its performance and operation comply with the prescribed requirements

**3.24****parallel measurement**

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

**3.25****performance characteristic**

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

**3.26****performance criterion**

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

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**EN 14625:2005 (E)****3.27****period of unattended operation**

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

**3.28****repeatability (of results of measurement)**

closeness of the agreement between the results of successive individual measurements of the same measurand carried out under the same conditions of measurement [1]

NOTE These conditions are called laboratory repeatability conditions and 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.

**3.29****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 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.

NOTE 2 In this document the reproducibility under field conditions is expressed as a value with a level of confidence of 95 %

**3.30****residence time inside the analyser**

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

**3.31****residence time in the sampling system**

time period for the sampled air to be transported from the sampling inlet (of the sampling system) to the inlet of the analyser

**3.32****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 90 % of the stable in output reading

**3.33****response time (fall)**

response time at a negative step change

NOTE Response time (fall) is the sum of the lag time (fall) and the fall time.

**3.34****response time (rise)**

response time at a positive step change

NOTE Response time (rise) is the sum of the lag time (rise) and the rise time.

**3.35****rise time**

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

**3.36****sampled air**

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

**3.37****sampling inlet**

entrance to the sampling system where ambient air is collected from the atmosphere

**3.38****short-term drift**

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

**3.39****standard uncertainty**

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

[ENV 13005]

**3.40****surrounding temperature**

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

**3.41****type approval**

decision taken by a designated body that the pattern of an analyser conforms to the requirements as laid down in this document

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**3.42****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

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**3.43****uncertainty(of measurement)**

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

**4 Symbols and abbreviated terms**

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

$A_a$	availability of the analyser
$A_v$	average concentration of the measurand during the field test
$b_{gp}$	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
$b_{gt}$	sensitivity coefficient of the analyser to sample gas temperature change
$b_{st}$	sensitivity coefficient of the analyser to surrounding air temperature change
$b_v$	sensitivity coefficient of the analyser to electrical voltage change
$C$	$O_3$ concentration of the applied gas
$C_{P_1}$	average concentration of the measurements at sampling gas pressure $P_1$

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$C_{P2}$	average concentration of the measurements at sampling gas pressure $P_2$
$C_{s,1}$	average concentration of the measurements at span level at the beginning of the drift period
$C_{s,2}$	average concentration of the measurements at span level at the end of the drift period
$c_t$	test gas concentration
$C_{T1}$	average concentration of the measurements at sample gas temperature $T_1$
$C_{T2}$	average concentration of the measurements at sample gas temperature $T_2$
$C_{V1}$	average concentration reading of the measurements at voltage $V_1$
$C_{V2}$	average concentration reading of the measurements at voltage $V_2$
$C_{z,1}$	average concentration of the measurements at zero at the beginning of the drift period
$C_{z,2}$	average concentration of the measurements at zero at the end of the drift period
$C_{\text{const}}^{\text{av}}$	average of at least four independent measurements during the constant concentration period ( $t_c$ )
$C_{\text{var}}^{\text{av}}$	average of at least four independent measurements during the variable concentration period ( $t_v$ )
$\overline{d}_f$	average difference of parallel measurements
$d_{f,i}$	the $i$ th difference in a parallel measurement
$D_{l,s}$	long-term drift at span concentration $c_t$
$D_{l,z}$	long-term drift at zero
$D_{s,s}$	short-term drift at span level
$D_{s,z}$	short-term drift at zero
$D_{\text{sc}}$	difference sample/calibration port
$E_{\text{ss}}$	sample system collection efficiency
$F_r$	response factor in concentration units per voltage output of the analyser
$P_1$	sampling gas pressure $P_1$
$P_2$	sampling gas pressure $P_2$
$R_d$	mean analyser response to the test gas directly sampled by the analyser
$r_f$	reproducibility under field conditions
$r_{f,\text{abs}}$	absolute reproducibility in the field
$R_m$	mean analyser response to the test gas via the sample manifold
$S_{r,z}$	repeatability standard deviation at zero
$S_{r,\text{ct}}$	repeatability standard deviation at concentration $c_t$

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$s_{r,f}$	reproducibility standard deviation under field conditions
$s_l$	repeatability standard deviation
$T$	surrounding air temperature
$T_1$	sample gas temperature $T_1$
$T_2$	sample gas temperature $T_2$
$t_d$	relative difference between response time (rise) and response time fall
$t_f$	response time (fall)
$t_l$	surrounding air temperature at the laboratory
$t_{n-1, 0,05}$	two-sided Students t-factor at a confidence level of 0,05, with $n-1$ degrees of freedom
$t_r$	response time (rise)
$t_t$	time period of the field test minus the time for calibration, conditioning and maintenance
$t_u$	total time period with validated measuring data
$t_v$	whole number of $t_{O_3}$ and $t_{zero}$ pairs
$V_1$	minimum voltage $V_{min}$ (V) specified by the manufacturer
$V_2$	maximum voltage $V_{max}$ (V) specified by the manufacturer
$\bar{x}$	average of measurements
$x_1$	first average of the measurements at $T_1$ just after calibration
$x_2$	second average of the measurements at $T_1$ just before calibration
$x_z$	average of the measurements at zero
$x_{ct}$	average of the measurements at concentration $c_t$
$x_{av}$	averaging effect
$x_c$	average of the measurements using the calibration port
$x_{H_2O,z,ct}$	influence quantity of $H_2O$ with concentration 19 mmol/mol
$x_i$	the $i$ th measurement
$x_{int,ct}$	influence quantity of the interferent at concentration $c_t$
$x_{int,z}$	influence quantity of the interferent at zero
$x_l$	lack of fit (largest residual from the linear regression function)
$x_s$	average of the measurements using the sample port
$x_s$	difference between the readings of the recent zero check and the most recent calibration
$x_T$	average of the measurements at $T_{min}$ or $T_{max}$

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$X_{\text{benx,z,ct}}$	influence quantity of benzene with concentration 1 $\mu\text{mol/mol}$
$X_z$	difference between the readings of two consecutive zero checks
$(X_{1,i})$	the $i$ th measurement result of analyser 1
$(X_{2,i})$	the $i$ th measurement result of analyser 2 at the same time as the measurement of analyser 1
$Z_1$	reading of the first zero check
$Z_2$	reading of the second zero check
$\Delta P_m$	measured pressure drop induced by the manifold pump
$\Delta R_a$	change in the analyser's response due to the influence of the pressure drop induced by the manifold pump, expressed as a percentage

**5 Principle****5.1 General**

This document describes the method for measurement of the concentration of ozone in ambient air by means of ultraviolet photometry. The requirements, the specific components, the ultraviolet photometric analyser and its sampling system are described. For the analyser a number of performance characteristics with associated minimum performance criteria are given. The actual values of these performance characteristics for a specific type of analyser have to 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 suitable analyser for a specific measuring task in the field is based on the calculation of the combined expanded uncertainty of the measuring method. In this combined expanded uncertainty calculation the actual values of the various performance characteristics of a type approved analyser and the site-specific conditions at the monitoring station are taken into account. The expanded uncertainty of the method shall meet the requirements of the (EU) legislation. For ongoing measurements in the field, requirements and recommendations for quality assurance and quality control are given (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.

**NOTE** 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 document test procedures are described for the determination of the actual values of the performance characteristics for at least two analysers in a laboratory and two analysers in the field. These tests shall be performed by a designated body. The type approval of an analyser is based on the calculation of the combined expanded uncertainty in the measurement result derived from the numerical values of the tested performance characteristics and compared to a prescribed maximum uncertainty.

The type approval of an analyser and subsequent OA and QC procedures provide evidence that the defined requirements concerning data quality laid out in relevant EU directives 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.

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 characteristics, 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.

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

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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 ultraviolet photometric analyser at a monitoring station, a single sampling inlet 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 equipment will contribute to the combined expanded uncertainty of the measurement; to minimise this contribution to the combined expanded uncertainty, performance criteria for the sampling equipment are given in the following subclauses.

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

### 6.2 Sampling location

The location where the ambient air is sampled and analysed is not specified, as this depends on the measurement requirements (such as measurements in e.g. a rural area or urban-background area).

NOTE For guidance on sampling points on a micro-scale, see Annex D.