

Ambient air quality — Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence

The European Standard EN 14212:2005 has the status of a
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National foreword

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The UK participation in its preparation was entrusted by Technical Committee EH/2, Air quality, to Subcommittee EH/2/3, Ambient atmospheres, which has the responsibility to:

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- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
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Ambient air quality - Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence

Qualité de l'air ambiant - Méthode normalisée pour le mesurage de la concentration de SO₂ par fluorescence UV

Luftqualität - Messverfahren zur Bestimmung der Konzentration von Schwefeldioxid mit Ultraviolett-Fluoreszenz

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Foreword

This document (EN 14212:2005) 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of an identical text or by endorsement, at the latest by September 2005, and conflicting national standards shall be withdrawn at the latest by September 2005.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.

1 Scope

This document specifies a continuous measurement method for the determination of the concentration of sulphur dioxide present in ambient air based on the ultraviolet fluorescence measuring principle. This document describes the performance characteristics and sets the relevant minimum criteria required to select an appropriate ultraviolet fluorescence 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 for use.

The method is applicable to the determination of the mass concentration of sulphur dioxide present in ambient air from $0 \mu\text{g}/\text{m}^3$ to $1\,000 \mu\text{g}/\text{m}^3$ sulphur dioxide. This concentration range represents the certification range for the type approval test.

NOTE 1 $0 \mu\text{g}/\text{m}^3$ to $1\,000 \mu\text{g}/\text{m}^3$ of SO_2 corresponds to 0 nmol/mol to 376 nmol/mol of SO_2 .

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

The method covers the determination of ambient air concentrations of sulphur dioxide in zones classified as rural areas, urban-background areas and traffic-orientated locations.

The results are expressed in $\mu\text{g}/\text{m}^3$ (at 293 K and 101,3 kPa).

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

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 6142, *Gas analysis — Preparation of calibration gas mixtures — Gravimetric method*

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

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

ISO 6145 (all parts), *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods*

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 air¹⁾

3.2

sample gas temperature

temperature at the sample inlet outside the monitoring station

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/IEC 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)

¹⁾ As stated in the relevant EU legislation.

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**lack of fit**

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

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**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 SO₂ analyser has been installed in such a way that its performance and operation comply with the prescribed requirements

3.23

parallel measurement

two 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 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..

3.28

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 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 %

3.29

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 output reading

3.30

response time (fall)

response time to a negative step change

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

3.31

response time (rise)

response time to a positive step change

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

3.32

rise time

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

3.33

sampled air

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

3.34

sampling inlet

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

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

[ENV 13005]

3.37

surrounding temperature

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

3.38

type approval

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

3.39

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

3.40

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

4 Symbols and abbreviated terms

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

A_a	availability of the analyser;
av	average concentration of the measurand during the field test;
b_{gp}	sensitivity coefficient of the analyser to sample gas pressure change;
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	SO ₂ concentration of the applied gas;
C_{P1}	average concentration of the measurements at sampling gas pressure P_1 ;
C_{P2}	average concentration of the measurements at sampling gas pressure P_2 ;
C_R	concentration of the reference standard;
C_s	concentration of site standard;
$C_{s,1}$	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_{sc}	difference sample/calibration port ^e ;
E_{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;

$r_{f,abs}$	absolute reproducibility in the field;
r_i	repeatability standard deviation;
$r_{i,ct}$	repeatability at concentration c_i ;
$r_{i,z}$	repeatability at zero;
R_m	mean analyser response to the test gas via the sample manifold;
$s_{r,z}$	repeatability standard deviation at zero;
$s_{r,ct}$	repeatability standard deviation at concentration c_i ;
$s_{r,f}$	reproducibility standard deviation under field conditions;
s_i	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 (K);
$t_{n-1, 0,05}$	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_{SO_2} 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;
V_r	voltage obtained when the reference standard is injected;
V_s	voltage obtained when the site standard is injected;
V_z	voltage obtained when zero gas is injected;
$\bar{X}$	average of measurements;
x_1	first average of the measurements at T_l just after calibration;
x_z	average of the measurements at zero;
x_2	second average of the measurements at T_l just before calibration;
x_{ct}	average of the measurements at concentration c_i ($\mu\text{mol/mol}$);

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;
$X_{H_2S,z,ct}$	influence quantity of H_2S with concentration 10 nmol/mol;
x_i	the i th measurement;
$X_{int,ct}$	influence quantity of the interferent at concentration c_i ($\mu\text{mol/mol}$);
$X_{int,z}$	influence quantity of the interferent at zero ($\mu\text{mol/mol}$);
X_l	lack of fit (largest residual from the linear regression function);
$X_{NH_3,z,ct}$	influence quantity of NH_3 with concentration 10 nmol/mol;
$X_{NO,z,ct}$	influence quantity of NO with concentration 500 nmol/mol;
$X_{NO_2,z,ct}$	influence quantity of NO_2 with concentration 200 nmol/mol;
X_{Psg}	influence quantity of sampling gas pressure;
x_s	average of the measurements using the sample port ($\mu\text{mol/mol}$);
X_s	difference between the readings of two consecutive span checks;
x_T	average of the measurements at T_{min} or T_{max} ;
$X_{xI,z,ct}$	influence quantity of m-xylene with concentration 1 $\mu\text{mol/mol}$;
X_z	difference between the readings of the recent zero check and the most recent calibration;
$(x_{1,f})_i$	the i th measurement result of analyser 1, mathematically corrected for zero and span drift;
$(x_{2,f})_i$	the i th measurement result of analyser 2 at the same time as the measurement of analyser 1, mathematically corrected for zero and span drift;
Z_1	reading of the first zero check;
Z_2	reading of the second zero check;
ΔP_m	measured pressure drop induced by the manifold pump;
ΔR_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 sulphur dioxide in ambient air by means of ultraviolet fluorescence. The requirements, the specific components of the ultraviolet fluorescence analyser and its sampling system are described. A number of performance characteristics with associated minimum performance criteria are given for the analyser. The actual values of these performance characteristics for a specific type of analyser shall be determined in a so-called type approval test for which procedures have been described. The type approval test comprises a laboratory and a field test. The selection of a type approval test

analyser for a specific measuring task in the field is based on the calculation of the combined expanded uncertainty of the measurement 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 combined expanded uncertainty of the method shall meet the requirements of the EU legislation. Requirements and recommendations for quality assurance and quality control are given for the measurements in the field (see 9.4).

5.2 Measuring principle

UV (ultraviolet) fluorescence is based on the emission of light by SO₂ molecules excited by UV radiation when they return to their ground state:

The first reaction step is:



Then in the second step the excited SO₂^{*} molecule returns to its ground state, emitting an energy hν' according to the reaction:



The intensity of the fluorescence radiation is proportional to the number of SO₂ molecules in the detection volume and is therefore proportional to the concentration of SO₂.

Therefore:

$$F = k \times c_{\text{SO}_2} \quad (3)$$

where

F is the intensity of fluorescence radiation;

k is the factor of proportionality;

c_{SO_2} is the concentration of SO₂.

Before entering the fluorescence analyser the air sample is passed through a filter in order to exclude interferences caused by contamination with particles.

The sampled air is scrubbed to remove any interference by aromatic hydrocarbons that may be present. A hydrocarbon scrubber device is used to achieve this.

The sampled air is then introduced into a reaction chamber, where it is irradiated by UV light in the wavelength range between 200 nm and 220 nm. The UV fluorescent light emitted in the wavelength range of 240 nm to 420 nm, is optically filtered and then converted to an electrical signal by a UV detector, for example, a photomultiplier tube.

The response of the analyser is proportional to the number of SO₂ molecules in the reaction chamber. Therefore, temperature and pressure either have to be kept constant, or, if variation of these parameters occurs, the measured values have to be corrected.

The concentration of sulphur dioxide is directly measured in volume/volume units if the analyser is calibrated using a volume/volume standard. The final results for reporting are expressed in µg/m³ 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 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 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.

5.4 Field operation and quality control

Prior to the installation and operation of a type approved analyser at a monitoring station, a 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.

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

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

6 Sampling equipment

6.1 General

Depending on the installation of the fluorescence 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 uncertainty of the measurement; to minimise this contribution to the uncertainty, performance criteria for the sampling equipment and sampling conditions are given in the following subclauses.

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

6.2 Sampling location

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

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

6.3 Sample inlet and sampling line

A specific method for sampling or sampling equipment is not described. It is acceptable that the equipment fulfils the following minimum requirements.

The sample inlet shall be constructed in such a way that ingress of rain water into the sampling system is prevented. The sampling line shall be as short as practicable to minimise the residence time.

The material of the sample inlet as well as the sampling line (or system) may 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. Copper or copper-based alloys, shall not be used. The influence of the sampling system on the measured concentrations of sulphur dioxide due to losses shall be less than 2 %

NOTE 1 This value may be achieved when the quality assurance and quality control recommendations are followed (see Clause 9).

NOTE 2 The sample line 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 due to the sampling line including the particulate filter shall be such that it causes less than 1 % of the output signal of the analyser.

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

Depending on the location of the particulate filter in the sampling system (see 6.4) the sampling line may be contaminated by deposition of dust. This may induce losses of SO₂ in the sampling line. The sampling system shall be cleaned (as stated in 9.4.2) with a frequency which is dependent on the site-specific conditions.

The sampling line, manifold and filter shall be conditioned (at initial installation and after each cleaning) to avoid temporary decrease of measured SO₂ concentrations. Both sampling line and filter shall be conditioned with ambient air for a period of at least 30 min at the nominal sampling flow rate. The concentration measured during these periods shall not be included in the calculation of data capture, hourly and annual averages.

These conditioning periods shall not be included in the calculation of the availability of the analyser during the type approval test (8.5.6) and during field operation (11.2.3). Conditioning may also be done in the laboratory before installing, in the sampling system.

6.4 Particulate filter

A particulate filter shall be placed in the sample line before the inlet of the analyser. This particulate 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 SO₂.

NOTE 1 A pore size of the filter of 5 µm usually fulfils this requirement.

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

The particulate filter shall be changed periodically depending on the dust loading at the sampling site (as indicated in 9.4.2). During this filter change the filter housing shall be cleaned. Overloading of the particulate filter may cause loss of sulphur dioxide by adsorption on the particulate matter and may increase the pressure drop in the sampling line.

6.5 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.

6.6 Sampling pump for the manifold

When a sampling manifold is used, a pump (or fan) is necessary for sampling ambient air and suction of the sampled air through the sampling manifold. The inlet of the sampling pump (or fan) 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 of a sample from inlet until entering the analyser is less than 5 s. To verify functioning of this pump, it is recommended that a flow alarm system is installed. 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 $< 1 \%$.

7 Analyser equipment

7.1 General

A schematic diagram of a UV fluorescence analyser is given in Annex D.

UV fluorescence analyser consists of the principal components which are described in 7.2 to 7.6.

7.2 Selective traps for interfering agents

One or more selective traps shall be used before the fluorescence cell to remove interfering gases such as aromatic hydrocarbons.

These selective traps shall not retain any SO_2 , and shall be changed regularly in accordance with the manufacturer's instruction manuals.

If high concentrations of H_2S are expected in the ambient air, a selective scrubber should be used.

7.3 Optical assembly

The optical assembly consists of a UV lamp, a fluorescence cell, a reference sensor and a UV detector.

The UV lamp emission may be pulsed electronically or mechanically in order to enable synchronous detection and amplification of the signal. The lamp shall have a stabilised power supply to ensure a stable emission of light. An optical filter is used to restrict the wavelengths to a range which allows excitation of the sulphur dioxide molecule and minimizes the interferences due to water vapour, aromatic hydrocarbons or nitrogen monoxide. This filter shall remove radiation at wavelengths longer than 600 nm, to minimize any interference produced by the UV fluorescence of unsaturated hydrocarbons, which radiate at these wavelengths.

The reference sensor in the extension of the beam path behind the reaction chamber checks the constancy of the UV lamp and is used to correct the fluorescence signal or to control the UV lamp.

The fluorescence cell shall be made of material inert to SO_2 and UV radiation. The cell shall be heated to a constant temperature above the water vapour dew point to avoid water condensation, and to minimise temperature changes. An optical trap in the fluorescence cell shall be used to prevent reflection of the UV radiation.

The UV detector, for example a photomultiplier tube, detects the fluorescence light emitted by the SO_2 molecules in the fluorescence cell. A selective optical filter placed in front of the photomultiplier tube reduces the signal due to scattering of incident light.

The optical assembly shall be placed in a heated temperature-controlled enclosure.

7.4 Pressure measurement

The output signal of the analyser is proportional to the density of SO_2 (number of SO_2 molecules) present in the reaction chamber and depends on the pressure in the chamber. Variations of internal pressure shall be measured and the signal corrected.

7.5 Flow rate indicator

A flow rate indicator shall be included in the analyser.

NOTE It is recommended that the flow rate be kept constant by means of a flow controller.

7.6 Sampling pump for the analyser

The sampling pump is situated at the outlet of the analyser, and draws the sample 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 reaction chamber.

NOTE If the use of the UV lamp produces ozone, it is recommended to vent this ozone outside the monitoring station and away from the sampling inlet. A suitable charcoal filter may be used for trapping ozone.

7.7 Internal span source

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

8 Type approval of sulphur dioxide UV fluorescence analysers

8.1 General

The determination of the concentration of sulphur dioxide in ambient air has to fulfil the requirement of a maximum uncertainty in the measured values, which is prescribed by EU legislation. In order to achieve an uncertainty less than (or equal to) this required uncertainty, the analyser has to fulfil all the criteria for a number of performance characteristics, which are given in this document. The values of the selected performance characteristics shall be evaluated by means of laboratory and field tests. By combining the values of the selected performance characteristics in an uncertainty calculation, a judgement can be made whether or not the analyser meets the criterion of maximum uncertainty prescribed by EU legislation.

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

A designated body shall perform the type approval tests. The type approval shall be awarded by or on behalf of the competent authority.

NOTE It is recommended that the designated body for the type approval test is accredited for these activities according to EN ISO/IEC 17025.

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.

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 and 8.5.

Table 1 — Relevant performance characteristics and criteria

No.	Performance characteristic	Symbol	Clause	Lab. test	Field test	Performance criterion for SO ₂
1	Repeatability standard deviation at zero	$s_{r,z}$	8.4.5	x		≤ 1,0 nmol/mol
2	Repeatability standard deviation at concentration c_i (at a level of the hourly limit value)	$s_{r,ct}$	8.4.5	x		≤ 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	X_l		x		≤ 4,0 % of the measured value ^b
3b	Residual at zero	$X_{l,z}$		x		≤ 5,0 nmol/mol
4	Sensitivity coefficient of sample gas pressure	b_{gp}	8.4.7	x		≤ 3,0 nmol/mol/kPa
5	Sensitivity coefficient of sample gas temperature	b_{gt}	8.4.8	x		≤ 1,0 nmol/mol/K
6	Sensitivity coefficient of surrounding temperature	b_{st}	8.4.9	x		≤ 1,0 nmol/mol/K
7	Sensitivity coefficient of electrical voltage	b_v	8.4.10	x		≤ 0,30 nmol/mol/V
8	Interferents at zero and concentration c_i (at a level of the hourly limit value) ^a		8.4.11			
8a	H ₂ O with concentration 19 mmol/mol ^b	$X_{H_2O,z,ct}$		x		≤ 10 nmol/mol
8b	H ₂ S with concentration 200 nmol/mol	$X_{H_2S,z,ct}$		x		≤ 5,0 nmol/mol
8c	NH ₃ with concentration 200 nmol/mol	$X_{NH_3,z,ct}$		x		≤ 5,0 nmol/mol
8d	NO with concentration 500 nmol/mol	$X_{NO,z,ct}$		x		≤ 5,0 nmol/mol
8e	NO ₂ with concentration 200 nmol/mol	$X_{NO_2,z,ct}$		x		≤ 5,0 nmol/mol
8f	m-xylene with concentration 1 µmol/mol	$X_{yl,z,ct}$		x		≤ 10,0 nmol/mol
9	Averaging effect	X_{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

No.	Performance characteristic	Symbol	Clause	Lab. test	Field test	Performance criterion for SO ₂
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 rise time and fall time	t_d	8.4.3	x		≤ 10 % relative difference or 10 s, whatever is the greatest
18	Difference sample/calibration port ^c	D_{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, but not less than 2 weeks
20	Availability of the analyser	A_a	8.5.7		x	> 90 %
^a performance criterion is set both at zero and span level ^b an H ₂ O-concentration of 19 mmol/mol is about 80 % RH at 293 K and 101,3 kPa ^c if relevant						
NOTE nmol/mol = ppb						

8.3 Design changes

The manufacturer shall report any (design) change of the previous type approved monitor to the competent authority. The underlying idea of the (design) change, as well as the expected consequences with respect to the performance characteristics as stated in Table 1, shall be reported by the manufacturer. The competent authority shall decide whether or not new tests are necessary. Excluded from reporting are changes in:

- material of the instrument frame (housing);
- electronic connectors;
- bolts, nuts, cable binders and other fixing materials.

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 document. The laboratory tests shall be performed on at least two analysers.

8.4.2 Test conditions

8.4.2.1 General

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

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

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.

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 to be demonstrated that the set value for the averaging time or the use of an active filter will not 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. All settings shall be noted down in the test report.

8.4.2.2 Parameters

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

Table 2 — Set points and stability of test parameters

Parameter	Set points	Stability
Sample gas pressure	Manufacturer's specification (except for the sample gas pressure test in, see 8.4.7)	$\pm 0,2$ kPa
Sample gas temperature	293 K – 296 K (except for the sample gas temperature test, see 8.4.8)	± 2 K
Surrounding temperature air	293 K – 296 K (except for the temperature of the surrounding air test, see 8.4.9)	± 2 K
Electrical voltage ^a	At nominal line voltage and within manufacturer's specification (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 ((synthetic) air containing a certain SO₂ concentration) traceable to national standards shall be used unless otherwise stated in this document. Various methods for the generation of test gases are given in Table 3.

Table 3 — Methods for preparation of calibration gases

Method	Description	Standard to be used
Cylinder	Gas cylinder (SO ₂ gas mixture in (synthetic) air)	ISO 6142 ISO 6143
Permeation tubes	Determination of the weight loss of a permeable tube containing SO ₂	ISO 6145-10
Static dilution	Preparation by means of injecting known amounts of SO ₂ into a known volume of air	ISO 6144
Dynamic dilution	Dynamic blending of cylinder gas with (synthetic) air	ISO 6145

The uncertainties in zero and span gases used for the laboratory and field tests shall be proven to be insignificant. Possible contamination of zero and span gas shall not significantly influence the results of the laboratory tests. Therefore the calibration gases and zero gas shall meet the following specifications:

Maximum permitted uncertainties in the concentration of gases used for laboratory tests: ± 3 %.

Specification of the purity of test gases and zero gas (expressed as absolute value) is given in Table 4.

Table 4a — Specification for purity of span gas

Pollutant	Concentration
H ₂ S	< 0,1 µmol/mol
NH ₃	< 2 nmol/mol
NO	< 1 nmol/mol
NO ₂	< 1 nmol/mol
m-xylene	< 0,05 nmol/mol
water	< 150 µmol/mol

Table 4b — Specification for purity of zero gas

Pollutant	Concentration
H ₂ S	< 0,1 µmol/mol
NH ₃	< 2 nmol/mol
NO	< 1 nmol/mol
NO ₂	< 1 nmol/mol
m-xylene	< 0,05 nmol/mol
water	< 150 µmol/mol
SO ₂	< 1 nmol/mol

NOTE It is advised to perform the field tests with the same set of cylinders and zero air generators, exclusively reserved for the tests. The stability of both the zero air and the 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.

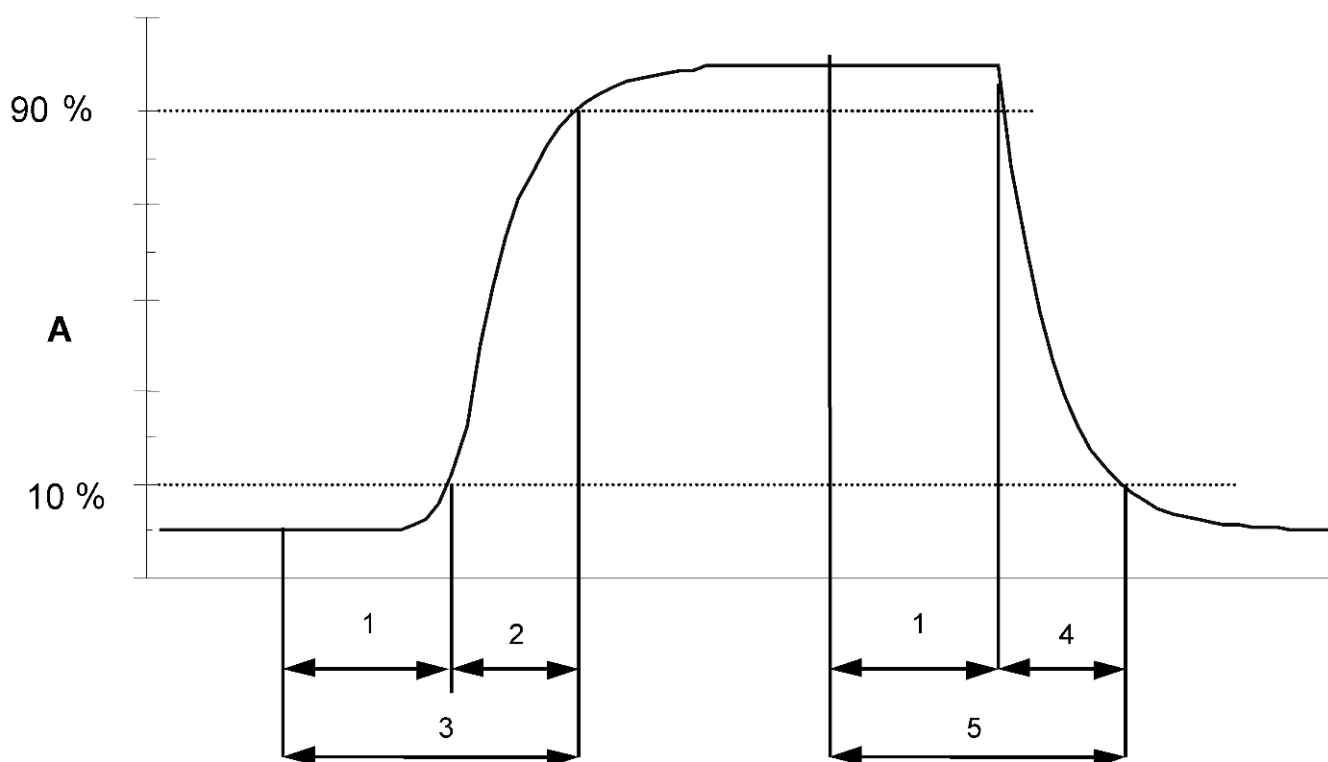
The sample flow rate shall be kept constant with the requirements as given in 8.4.2 ($\pm 1\%$) during the test.

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 approximately 80 % of the maximum of the certification range and vice versa (see Figure 1).

The change from zero gas to span gas needs to be made almost instantly with use of a suitable valve. The valve outlet shall be mounted direct to the inlet of the monitor, and both zero gas and span gas shall have the same “oversupply” which is vented with 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 monitor 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 of 98 % of the applied concentration has been reached, the span gas can be changed to zero again, and this event is the start ($t = 0$) of the (fall) lag time. When the reading of 2 % of the applied concentration has been reached the whole cycle as shown in Figure 1 is complete.

The elapsed time (response time) between the start of the step change and reaching of 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 the four response times (fall) shall be calculated.



Key

- A Analyser response
- 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 relative difference in response times shall be calculated according to:

$$t_d = \left| \frac{t_r - t_f}{t_r} \right| \times 100\% \quad (4)$$

where

t_d is the relative difference between response time (rise) and response time (fall) (%);

t_r is the response time (rise) (average of 4 measurements) (s);

t_f is the response time (fall) (average of 4 measurements) (s).

t_r , t_f , t_d , shall comply with the performance criterion 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). 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) whilst 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:

$$D_{s,z} = (C_{z,2} - C_{z,1}) \quad (5)$$

where

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

$C_{z,1}$ is the average of the zero gas measurements at the beginning of the drift period (just after calibration) (nmol/mol);

$C_{z,2}$ is the average of the zero gas measurements at the end of the drift period (12 h) (nmol/mol).

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

$$D_{s,s} = (C_{s,2} - C_{s,1}) - D_{s,z} \quad (6)$$

where

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

$C_{s,1}$ is the average of the span gas measurements at the beginning of the drift period (just after calibration) (nmol/mol);

$C_{s,2}$ is the average of the span gas measurements at the end of the drift period (12 h) (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 limit value shall be recorded.

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

$$s_r = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}} \quad (7)$$

where

s_r is the repeatability standard deviation (nmol/mol);

x_i is the i th measurement (nmol/mol);

$\bar{x}$ is the average of the 20 measurements (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 limit value).

8.4.6 Lack of fit

The lack of fit of the analyser shall be tested over the range between 0 % to 95 % of the maximum of the certification range using at least six concentrations (including the zero point). The analyser shall be adjusted at a concentration of about 90 % of the maximum of the certification range. At each concentration (including zero) at least five independent readings 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 X_1 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 limit value shall be taken in the calculation of type approval requirement 2 and 4.

8.4.7 Sensitivity coefficient of sample gas pressure

Measurements are taken at a concentration of about 70 % to 80 % of the maximum of the certification range at an absolute pressure of about 80 kPa $\pm$ 0,2 kPa and at an absolute pressure of about 110 kPa $\pm$ 0,2 kPa. At each pressure after waiting the time equivalent to one independent reading three individual measurements are recorded. From these 3 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:

$$b_{gp} = \left| \frac{(C_{p_1} - C_{p_2})}{(P_2 - P_1)} \right| \quad (8)$$

where

b_{gp} is the sample gas pressure influence (nmol/mol/kPa);

C_{p_1} is the average concentration of the measurements at sampling gas pressure P_1 (nmol/mol);

C_{p_2} is the average concentration of the measurements at sampling gas pressure P_2 (nmol/mol);

P_1 is the sampling gas pressure P_1 (kPa);

P_2 is the sampling gas pressure P_2 (kPa).

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

8.4.8 Sensitivity coefficient of sample gas temperature

For the determination of the dependence of the sample gas temperature measurements shall be performed at sample gas temperatures of $T_1 = 0\text{ °C}$ and $T_2 = 30\text{ °C}$. The temperature dependence shall be determined at a concentration of about 70 % to 80 % of the maximum of the certification range. Wait the time equivalent to one independent reading and then record 3 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:

$$b_{gt} = \frac{(C_{T_2} - C_{T_1})}{(T_2 - T_1)} \quad (9)$$

where

b_{gt} is the sample gas temperature influence ($\mu\text{mol/mol/K}$) in nmol/mol/K ;

C_{T_1} is the average concentration of the measurements at sample gas temperature T_1 (nmol/mol);

C_{T_2} is the average concentration of the measurements at sample gas temperature T_2 (nmol/mol);

T_1 is the sample gas temperature T_1 (K);

T_2 is the sample gas temperature T_2 (K).

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

8.4.9 Sensitivity coefficient of the surrounding temperature

The influence of the surrounding temperature shall be determined at the following temperatures (within the specifications of the manufacturer):

- 1) at the minimum temperature $T_{\min} = 273\text{ K}$;
- 2) at the laboratory temperature (T_l), see 8.4.2.2;
- 3) at the maximum temperature $T_{\max} = 303\text{ K}$.

For these tests a climate chamber is necessary.

The influence shall be determined at a concentration around 70 % to 80 % of the maximum of the certification range. At each temperature setting after waiting the time equivalent to one independent reading three independent 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 measurements shall be performed in the following sequence of the temperature settings:

T_l , $T_{\min}$, T_l and T_l , $T_{\max}$, T_l

At the first temperature (T_1) 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 measurement at T_1 , at $T_{\min}$ and again at T_1 . This procedure shall be repeated at the temperature sequence of T_1 , $T_{\max}$, and at T_1 .

In order to exclude any possible drift due to factors other than temperature, the measurements at T_1 are averaged, which is taken into account in the following formula for calculation of the surrounding air temperature dependence:

$$b_{\text{st}} = \left| \frac{x_T \times \frac{x_1 + x_2}{2}}{T \times T_1} \right| \quad (10)$$

where

- b_{st} is the surrounding air temperature dependence at zero or span and at $T_{\min}$ or $T_{\max}$ (nmol/mol/K);
- x_T is the average of the measurements at $T_{\min}$ or $T_{\max}$ (nmol/mol);
- x_1 is the first average of the measurements at T_1 just after calibration (nmol/mol);
- x_2 is the second average of the measurements at T_1 just before calibration (nmol/mol);
- T_1 is the surrounding air temperature at the laboratory (K);
- T is the surrounding air temperature $T_{\min}$ or $T_{\max}$ (K).

For reporting the surrounding air temperature dependence the highest value is taken of the two calculations of the temperature dependence at $T_{\min}$ and $T_{\max}$.

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

8.4.10 Sensitivity coefficient of electrical voltage

The sensitivity coefficient of electrical voltage shall be determined at both ends of the specified voltage range, $V_{\min}$ and $V_{\max}$ at zero concentration and at a concentration around 70 % to 80 % of the maximum of the certification range. 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:

$$b_v = \frac{(C_{V_2} - C_{V_1})}{(V_2 - V_1)} \quad (11)$$

where

- b_v is the voltage influence (nmol/mol/V);
- C_{V_1} is the average concentration reading of the measurements at voltage V_1 (nmol/molV);
- C_{V_2} is the average concentration reading of the measurements at voltage V_2 (nmol/molV);
- V_1 is the minimum voltage $V_{\min}$ (V) specified by the manufacturer;
- V_2 is the maximum voltage $V_{\max}$ (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 Interferences

The analyser response to certain interferences which are to be expected to be present in ambient air shall be tested. The interferences 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 limit value.

The concentration of the mixtures of the test gases with the interferent shall have an uncertainty of less than 5 % and shall be traceable to national standards. The interferences 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:

$$X_{\text{int},z} = x_z \quad (12)$$

$$X_{\text{int},c_t} = x_{c_t} - c_t \quad (13)$$

where

$X_{\text{int},z}$ is the influence quantity of the interferent at zero (nmol/mol);

x_z is the average of the measurements at zero (nmol/mol).

X_{int,c_t} is the influence quantity of the interferent at concentration c_t (nmol/mol);

x_{c_t} is the average of the measurements at concentration c_t (nmol/mol);

c_t is the concentration of the applied gas at the level of the hourly limit value (nmol/mol).

The influence quantity of the interferences 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 also Figure 2):

- a stepwise varied concentration of SO_2 between zero and concentration c_t (70 % to 80 % of the maximum of the certification range).

The time period (t_c) of the constant SO₂ concentration shall be at least equal to a period necessary to obtain four independent readings (which equals at least 16 response times). The time period (t_v) of the varying SO₂ concentration shall be at least equal to a period to obtain four independent readings. The time period (t_{SO_2}) for the SO₂ concentration shall be 45 s. followed by a period (t_{zero}) of 45 s. of zero concentration. Further:

c_t is the test concentration (nmol/mol);

t_v is a whole number of t_{SO_2} and t_{zero} pairs, and contains a minimum of three such pairs.

The change from t_{SO_2} 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 (X_{av}) is calculated according to:

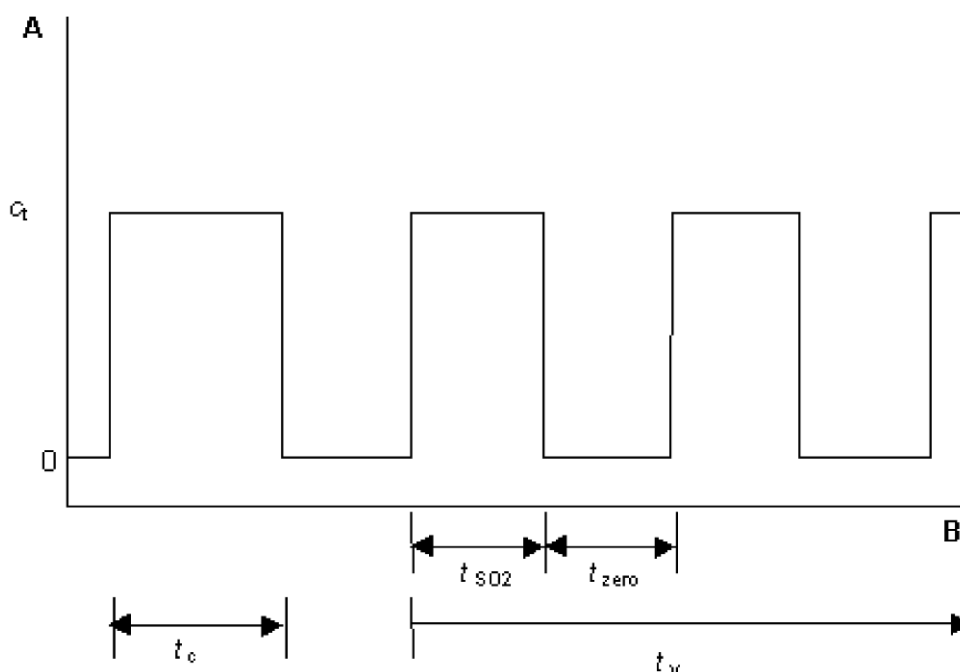
$$X_{\text{av}} = \frac{C_{\text{const}}^{\text{av}} - 2C_{\text{var}}^{\text{av}}}{C_{\text{const}}^{\text{av}}} \times 100\% \quad (14)$$

where

X_{av} is the averaging effect (%);

$C_{\text{const}}^{\text{av}}$ is the average of at least four independent measurements during the constant concentration period (t_c) (nmol/mol);

$C_{\text{var}}^{\text{av}}$ is the average of at least four independent measurements during the variable concentration period (t_v) (nmol/mol).



Key

A Concentration (nmol/mol)

B Time

Figure 2 — Concentration variations for the averaging effect test

8.4.13 Difference sample/calibration port

If the analyser has different ports for feeding sample gas and calibration gas the difference in response of the analyser to feeding through the sample or calibration port shall be tested. The test shall be carried out by feeding the analyser with a test gas with a concentration of 70 % to 80 % of the maximum of the certification range through the sample port. The test shall consist of one independent followed by two individual measurements. After a period of at least 4 response times the test shall be repeated using the calibration port. The difference shall be calculated according to:

$$D_{sc} = \frac{x_s - x_c}{c_t} \times 100 \% \quad (15)$$

where

- D_{sc} is the difference sample/calibration port (%);
- x_s is the average of the measured concentrations using the sample port (nmol/mol);
- x_c is the average of the measured concentrations using the calibration port (nmol/mol);
- c_t is the concentration of the test gas (nmol/mol).

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

8.5 Determination of the performance characteristics during the field test

8.5.1 General

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

In the field test during a period of three months 2 analysers are tested for availability (period of unattended operation), reproducibility in the field and long-term drift. The analysers are run in parallel at one and the same sampling point at a selected monitoring station with specific ambient air conditions (8.5.2). Operational requirements are given for the correct determination of the long-term drift and the reproducibility under field conditions (8.5.3).

8.5.2 Selection of a monitoring station for the field test

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

Location:

- traffic orientated station (4 m to 5 m from kerb-side).

Monitoring station facilities:

- sufficient capacity of the sampling manifold;
- enough room to place two analysers with calibration gases and/or calibration facilities;
- surrounding temperature control for the analysers, climate controlled at $293 \text{ K} \pm 4 \text{ K}$ with temperature registration;
- stable electrical voltage.

Other items that could be considered:

- presence of telemetry/telephone facilities for remote surveillance of the functioning of the equipment;
- accessibility.