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Ambient air — Determination of sulfur dioxide — Ultraviolet fluorescence method

Air ambiant — Dosage du dioxyde de soufre — Méthode par fluorescence dans l'ultraviolet

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ISO 10498:2004(E)

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ISO 10498 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 3, *Ambient atmospheres*.

INTERNATIONAL STANDARD **ISO 10498:2004(E)**

Ambient air — Determination of sulfur dioxide — Ultraviolet fluorescence method

1 Scope

This International Standard describes an ultraviolet fluorescence method for sampling and determining sulfur dioxide (SO_2) concentrations in the ambient air using automatic analysers.

This International Standard is applicable to the determination of sulfur dioxide mass concentrations of a few micrograms per cubic metre to a few milligrams per cubic metre or, expressed in terms of volume fraction, from a few microlitres per cubic metre to a few millilitres per cubic metre.

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.

ISO 4219, *Air quality — Determination of gaseous sulfur compounds in ambient air — Sampling equipment*

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

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

ISO 6145-1, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 1: Methods of calibration*

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

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

ISO 6349, *Gas analysis — Preparation of calibration gas mixtures — Permeation method*

ISO 6767, *Ambient air — Determination of the mass concentration of sulfur dioxide — Tetrachloromercurate (TCM)/pararosaniline method*

ISO 9169, *Air quality — Definition and determination of performance characteristics of an automatic measuring system*

3 Principle of analysis

The UV fluorescence method is not an absolute measurement method. Therefore, the instrument shall be calibrated regularly, using calibration gas diluted with air whose O_2 and N_2 content is close to normal atmospheric concentrations. It is also sensitive to pressure and temperature. This measurement technique is subject to less chemical interference than other techniques available at present (see Annex A). However, the following compounds can affect the determination of sulfur dioxide: hydrogen sulfide, aromatic hydrocarbons, nitric oxide, water, and low molecular mass mercaptans.

In individual cases where high concentrations of various pollutants are present, it is recommended that their effect on the response of the analyser be determined (see Annex A for typical interference factors).

The UV fluorescence method is based on the fluorescent emission of light by SO_2 molecules previously excited by UV radiation.

The first reaction step is:

$$SO_2 + h\nu(UV) \rightarrow SO_2^*$$

Then in the second step, the excited SO_2^* molecule returns to the original ground state, emitting a photon of energy $h\nu'$ according to the reaction:

$$SO_2^* \rightarrow SO_2 + h\nu'$$

The intensity of the fluorescent radiation is proportional to the number of SO_2 molecules in the detection volume, and is therefore proportional to the molar concentration of SO_2.

Therefore:

$$I = k[SO_2]$$

where

I is the intensity of fluorescent radiation;

k is the factor of proportionality;

$[SO_2]$ is the molar concentration of SO_2.

The air sample flows into the inlet of the analyser, where it is scrubbed to remove any interference by aromatic hydrocarbons that may be present. A hydrocarbon scrubber device usually accomplishes this.

Then the air sample flows into a reaction chamber, where it is irradiated by UV radiation with a wavelength in the range of 200 nm to 220 nm.

The fluorescent light, in the wavelength range of 240 nm to 420 nm, is optically filtered and then converted to an electrical signal by a detector, for example a photomultiplier tube.

The response of the analyser is proportional to the number of SO_2 molecules in the reaction chamber. Therefore, temperature and pressure either have to be kept constant or, if variation of these parameters is expected, the measured values have to be corrected.

For this UV fluorescence method to yield accurate concentration measurements, it must be calibrated against some primary standard (see 4.2).

4 Reagents and materials

4.1 Zero air

Zero air used in the calibration of the analyser should not contain a concentration of SO_2 detectable by the analyser under calibration. The concentration of O_2 in the zero air shall be within ± 2 % of that in normal air (20,9 %).

4.2 SO_2 calibration gas mixtures

4.2.1 Primary calibration method

One of the following equivalent methods for primary calibration shall be used:

- static volumetric dilution (ISO 6144);
- permeation tube sources (ISO 6349);
- tetrachloromercurate method (TCM) (ISO 6767);
- gravimetric preparation of gas mixtures in combination with various dilution systems (ISO 6142, ISO 6145-1, ISO 6145-4, ISO 6145-6).

Several methods for generating SO_2 calibration gas standard mixtures are proposed (see 4.2.2). Whichever method is chosen, it is recommended that it be compared periodically against another independent traceable calibration method. The range of SO_2 calibration concentrations chosen shall be between 10 % to 90 % of the SO_2 concentration range in use.

4.2.2 Transfer-standard calibration methods

Other methods to prepare calibration standard gases may also be used, if they are comparable to one or more of the methods mentioned in 4.2.1.

Although any of the primary calibration methods may be used as transfer standards, in practice, it is easier to use a laboratory-calibrated permeation source or cylinder of SO_2. The latter can be used either directly (with cylinders containing 0,1 mg/m^3 to 10,0 mg/m^3 of SO_2 in air), or with appropriate quantitative dilution (using cylinders containing ten to several hundred milligrams of SO_2 per cubic metre of air).

Gas cylinders containing SO_2 standards shall be made of an inert material or have been passivated to ensure concentration stability of ± 3 % for the period of use expected. Cylinders containing low concentrations shall be checked regularly against primary standards.

4.2.3 Operational (field) span check

To aid in the quality control of the routine operation of the analyser on-site, span checks may be performed regularly (preferably daily, but at least weekly). For example, an internal permeation device may form an integral part of the apparatus, or an external calibrated cylinder, with appropriate dilution if necessary, may be used. The operation of the span check is controlled by valves, either manually or by remote control.

The described span-check system is suitable for quality control in routine operations (see for example ISO 6879), to verify that the analyser is operating correctly, but may not be suitable for proper calibration as described in 4.2.1. The span-check system should regularly be compared to a laboratory-based calibration system as described in 4.2.1.

5 Apparatus

5.1 Sampling line

The sampling line and its residence time shall be as short as practical. This line shall be of a material which is chemically inert to SO_2, such as fluorocarbon polymer or glass, in accordance with ISO 4219. If any doubt exists as to the inertness of the sampling line, calibration gases shall be used to test the complete sampling train.

If water is expected to condense in the sampling line (when humid ambient air is drawn into a cool measurement environment), auxiliary heating of the sampling line will be necessary.

5.2 Sample inlet filter for particulate matter

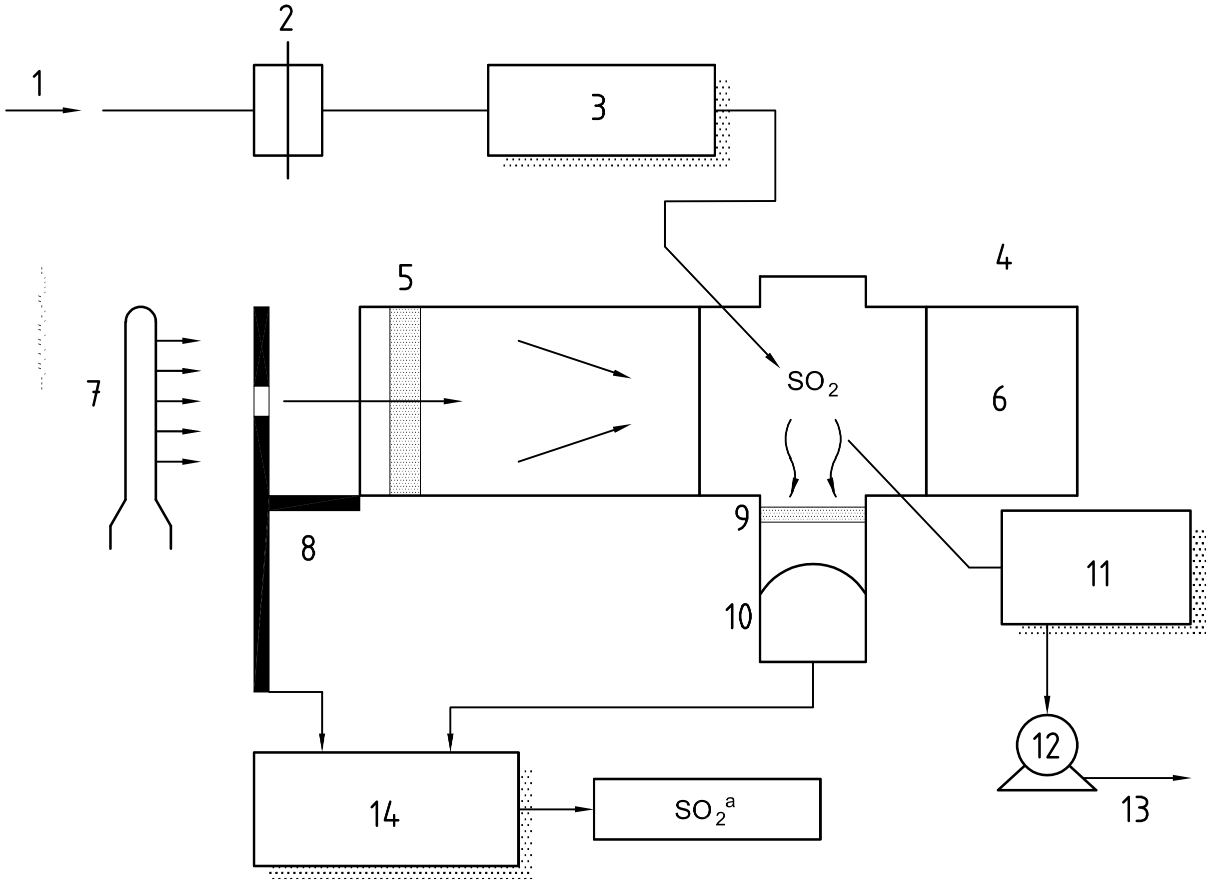
The particulate matter filter at the sample inlet shall remove particles which could interfere with the correct operation of the analyser. It shall not remove any SO_2, and consequently the filter and its support shall be made from inert material, such as fluorocarbon polymer.

It is recommended to install the filter at the inlet of the sampling line leading to the instrument in order to prevent contamination of the sampling component by ambient particulate matter.

NOTE A fluorocarbon polymer filter of 5 µm pore size has been found to be effective (see ISO 4219). Monthly replacement of filters loaded with particulate matter is generally sufficient. Depending on the concentration of suspended particulate matter in ambient air, the filter may need to be replaced more frequently.

5.3 Analyser for measuring SO_2 by UV fluorescence (see Figure 1).

The main components are described below.



Key

1	sample	8	modulator
2	sampling inlet filter	9	optical outlet filter
3	selective traps for interfering agents	10	photomultiplier tube
4	reaction chamber	11	compensation pressure flowrate
5	optical inlet filter	12	pump
6	optical trap	13	exhaust
7	UV lamp	14	synchronous electronic amplification

[a] Expressed as ml/m^3.

Figure 1 — Schematic diagram of a UV fluorescence SO_2 analyser

5.3.1 Selective traps for interferents

One or more selective traps should be used before the reaction chamber to remove interfering gases such as aromatic hydrocarbons.

These selective traps shall not retain any SO_2 and shall be changed in accordance with manufacturer's instruction manuals and existing national requirements.

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

5.3.2 Optical assembly and fluorescence cell

The UV lamp emission may be pulsed electronically or mechanically for synchronous detection and amplification of the signal.

The lamp shall have a stabilized power supply to ensure a stable emission of light. An optical filter is used to restrict the wavelengths to a range that allows excitation of the SO_2 molecule and yet minimizes the interference of water vapour, aromatic hydrocarbons or nitric oxide.

The detector, for example the photomultiplier tube, detects the fluorescent light emitted by the SO_2 molecules in the reaction chamber.

A selective optical filter placed in front of the detector reduces the signal due to scattering of the incident light.

The reaction chamber shall be made of material inert to SO_2 and UV radiation. The cell should be heated above the dewpoint to avoid water condensation and temperature fluctuations. The optical trap of the chamber prevents reflection of the exciting UV radiation.

The optical assembly should be placed in a heated enclosure.

5.3.3 Pressure regulator

The output signal of the analyser depends on the density of SO_2 (number of SO_2 molecules) present in the reaction chamber, and is therefore proportional to the pressure in the reaction chamber. Variations of internal pressure shall be measured and the signal corrected or controlled by means of a regulator.

The signal may have to be corrected also for external pressure and temperature fluctuations. Significant pressure corrections may be needed due to synoptic meteorological changes (up to ± 3 %) or by the altitude of the measurement site (about 10 % decrease in pressure for an 800 m rise in altitude).

NOTE One of the main causes of a reduction in pressure in the reaction chamber is a pressure drop in the sample line.

5.3.4 Flowrate controller and indicator

It is recommended that the flowrate be kept constant by means of a flowrate controller. A flowrate indicator should be included in the instrument.

5.3.5 Air pump, which draws air through the analyser, at the end of the sample flow path.

As the use of the UV lamp produces ozone, it is recommended to vent the analyser air through a suitable charcoal scrubber.

6 Procedure

6.1 Operation of the ambient-air SO_2 analyser

Install the instrument in a suitable location. Follow the manufacturer's operating instructions to set the various parameters correctly, including intensity of the UV source lamp, sample flowrate and (if applicable) the activation of the electronic temperature/pressure compensation.

Check to ensure that the manufacturer's performance specifications are met or exceeded. If necessary, the location shall also be temperature-controlled so as to minimize the effect of the temperature dependence of the instrument.

Sample the ambient air through the instrument and record the SO_2 concentration by means of a suitable recording device (for example chart recorder, electronic data acquisition system, etc.).

During continuous operation of the instrument, checks of the instrument zero, span and operational parameters shall be made at least once a week.

In order to ensure optimum analyser performance, follow the maintenance schedule as detailed in the manufacturer's instruction manual. It is recommended that the analyser be fully serviced either every six months or annually, as appropriate, based on the performance of the analyser. A full calibration of the instrument should be carried out before and after this service.

6.2 Calibration of the ambient-air SO_2 analyser

6.2.1 Principle

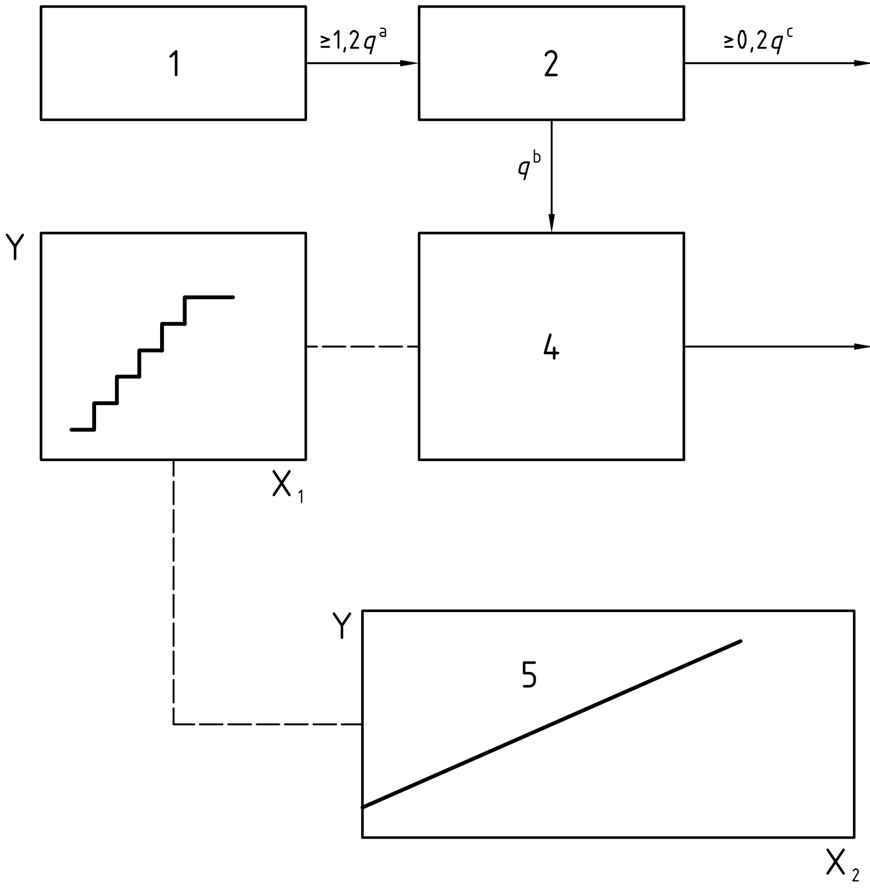
During the calibration procedure, operate the ambient-air SO_2 analyser at its normal flowrate and temperature.

The calibration shall include measurements of zero air (see 4.1), span gas, and at least five SO_2 concentrations (using a primary calibration gas standard described in 4.2.1) which shall be spaced to cover the ambient temperature range.

For all calibrations, the flow of calibration gases to the manifold shall exceed, by at least 20 %, the total flow required by the instrument attached to the manifold, with the excess appropriately vented at atmospheric pressure.

A schematic diagram of a calibration system is shown in Figure 2.

Alternatively, a transfer-standard calibration method can be calibrated against the SO_2 primary standard and then used to calibrate the ambient analyser at the sampling location.



Key

1	gas standard calibration source	Y	output
2	manifold	X_1	time
3	exhaust	X_2	SO_2 concentration
4	SO_2 analyser		
5	calibration curve		

[a] Flowrate.

[b] Sample flowrate.

[c] Excess flowrate.

Figure 2 — Schematic diagram of a calibration system

6.2.2 Calibration procedure

Carry out the calibration using the following procedure.

a) Assemble the apparatus as shown in Figure 2. For SO_2 analysers with automatic electronic temperature and pressure compensation, ensure that this circuit has been activated to yield corrected output values. For analysers without these compensations, measure and record the temperature of the reaction chamber and its internal pressure.

b) Introduce zero air into the manifold. If necessary, change the zero control setting of the SO_2 analyser to indicate an output reading close or equal to zero.

c) Record the output values of the SO_2 analyser.

d) Adjust the calibration source to produce the SO_2 concentration required for the span control setting. This concentration can be between 50 % to 100 % of the analyser full-scale reading, or of the expected SO_2 concentration range of the ambient air. If necessary, change the span control setting of the SO_2 analyser to indicate an output reading close or equal to the concentration produced.

e) Record the output values of the SO_2 analyser.

f) Repeat step b); if the span and zero settings are not independent, then the foregoing sequence of steps b) to e) must be repeated.

g) Adjust the calibration source to produce five additional SO_2 concentrations over the measurement range and record the output values without changing the span setting.

h) Plot the SO_2 analyser output values obtained in steps f) and g) versus the concentrations used.

i) Determine the calibration line of the analyser by means of a single linear regression or in accordance with ISO 9169.

Optionally, the procedure described above can be repeated if determinations of precision and accuracy are required.

6.2.3 Field calibration procedure using a transfer standard

A two-point calibration (zero gas and one upscale span point) of the analyser with a transfer standard calibrated previously against a reference calibration system is acceptable in field conditions. In this case, follow the steps b) to f) described in 6.2.2.

A three-point calibration (including zero and two span gases evenly spaced along the measurement scale) may be used for a field-check of linearity.

7 Expression of results

Record the output signal for the air sample to be measured.

Determine the corresponding concentration by using the appropriate calibration function obtained in 6.2.2.

Report the result in micrograms per cubic metre or milligrams per cubic metre, or the equivalent volume fraction.

The equation to be used for converting millilitres per cubic metre into milligrams per cubic metre, is as follows:

$$\rho_1 = \frac{\varphi_2 \times 64 \times 298 \times p}{24{,}459 \times T \times 1\,013}$$

where

ρ_1	is the mass concentration of SO_2, expressed in mg/m^3;
φ_2	is the volume fraction of SO_2, expressed in ml/m^3;
64	is the molar mass of SO_2, expressed in g/mol;
298	is the reference absolute temperature, expressed in kelvin;
p	is the measured gas pressure, expressed in hPa;
24,459	is the volume of 1 mol of gas, expressed in litres, at 298 K and 1 013 hPa;
T	is the measured temperature, expressed in kelvin;
1 013	is the reference gas pressure, expressed in hPa.

Annex A

(informative)

Typical performance characteristics of a commercial SO_2 analyser using UV fluorescence

The values indicated below are given for information only, as the actual characteristics may differ according to the instrument.

The characteristics mentioned are taken from the terms defined in ISO 6879 and ISO 9169.

- response time: about 2 min;
- zero drift: ranging from a negligible value to 5 µl/l per week;
- span drift: about 1 % (in relative terms) per day estimated over 7 days;
- repeatability: 1 % at about 50 µl/m^3;
- memory effect: on the order of a few µl/m^3 after sampling air with several ml/m^3 SO_2, stabilizes after about 15 min;
- linearity: the error may reach about 2 % between 50 µl/m^3 and 500 µl/m^3;
- selectivity: expressed in terms of the concentration of interfering agents which produces a variation of the output signal equal to 1 µl/m^3.
  - H_2S: negligible after scrubber;
  - CH_4: 3 300 ml/m^3;
  - NO: 100 µl/m^3;
  - water;
  - aromatic hydrocarbons;
  - $C_6H_5CH{=}CH$: 2 ml/m^3;
- temperature dependence: variation of the output signal is less than 2 % between sampling-gas temperatures 10 °C and 40 °C.

Bibliography

[1] ISO 6879, *Air quality — Performance characteristics and related concepts for air quality measuring methods*

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