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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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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

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

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:

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

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

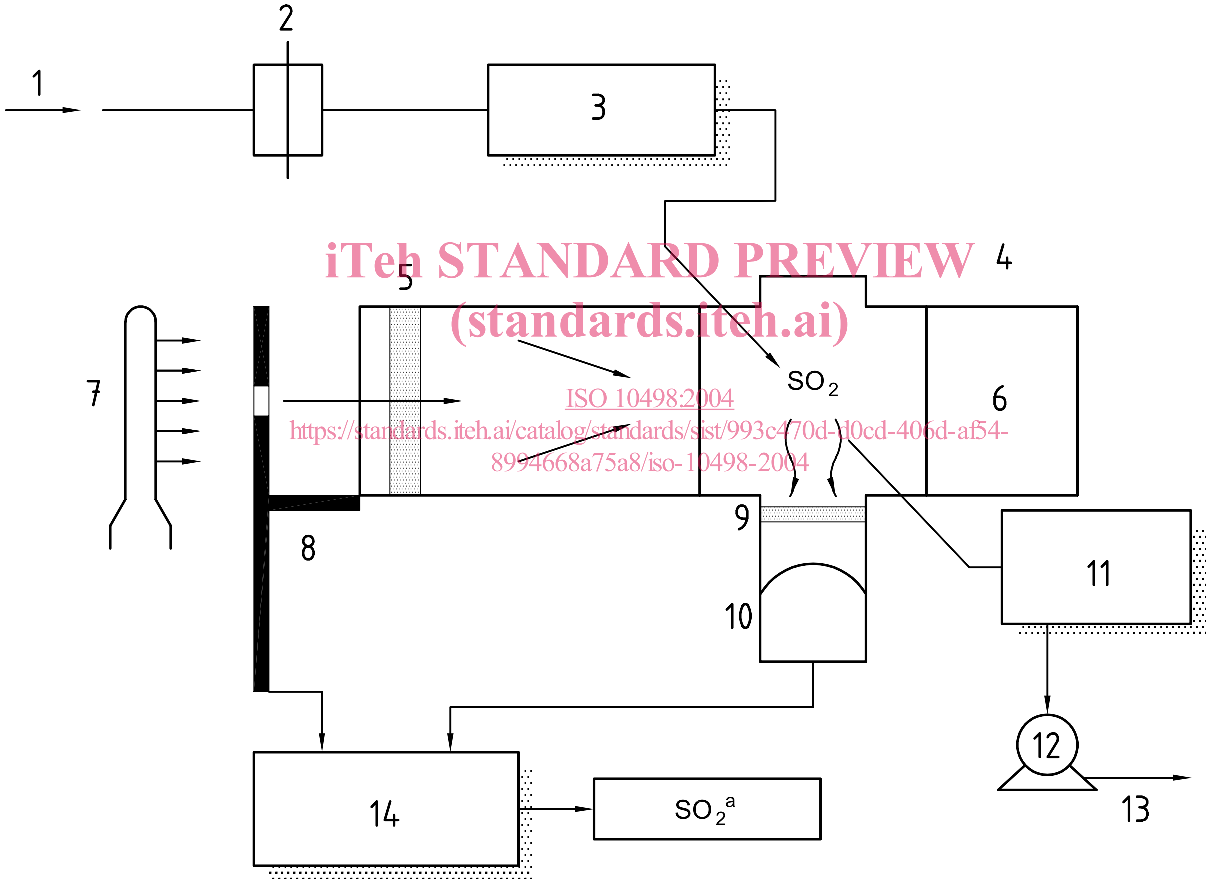
The particulate matter filter at the sample inlet shall remove particles which could interfere with the correct operation of the analyser. It shall not remove any SO_2, and consequently the filter and its support shall be made from inert material, such as fluorocarbon polymer.

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