



**SLOVENSKI STANDARD**  
**SIST ISO 10498:2004**

**01-december-2004**

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**Ni bUb]nfU\_`E8c`c Yj Ub^YjYd`cj Y[ UX]c\_g]XUÈ`A YtcXUi `fUj ]`c`] bY  
Zi cfYgWbWY**

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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**ICS:**

13.040.20      Kakovost okoljskega zraka      Ambient atmospheres

**SIST ISO 10498:2004**

**en,fr**

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INTERNATIONAL  
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ISO  
10498

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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

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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*.

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# 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<sub>2</sub>) 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)/parosaniline 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<sub>2</sub> and N<sub>2</sub> 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

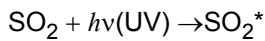
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following compounds can affect the determination of sulfur dioxide: hydrogen sulfide, aromatic hydrocarbons, nitric oxide, water, and low molecular mass mercaptans.

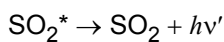
In individual cases where high concentrations of various pollutants are present, it is recommended that their effect on the response of the analyser be determined (see Annex A for typical interference factors).

The UV fluorescence method is based on the fluorescent emission of light by SO<sub>2</sub> molecules previously excited by UV radiation.

The first reaction step is:



Then in the second step, the excited SO<sub>2</sub>\* molecule returns to the original ground state, emitting a photon of energy  $h\nu'$  according to the reaction:



The intensity of the fluorescent radiation is proportional to the number of SO<sub>2</sub> molecules in the detection volume, and is therefore proportional to the molar concentration of SO<sub>2</sub>.

Therefore:

$$I = k[\text{SO}_2]$$

where

$I$  is the intensity of fluorescent radiation;

$k$  is the factor of proportionality;

$[\text{SO}_2]$  is the molar concentration of SO<sub>2</sub>.

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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<sub>2</sub> 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<sub>2</sub> detectable by the analyser under calibration. The concentration of O<sub>2</sub> in the zero air shall be within  $\pm 2\%$  of that in normal air (20,9 %).



## 4.2 SO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> calibration concentrations chosen shall be between 10 % to 90 % of the SO<sub>2</sub> 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<sub>2</sub>. The latter can be used either directly (with cylinders containing 0,1 mg/m<sup>3</sup> to 10,0 mg/m<sup>3</sup> of SO<sub>2</sub> in air), or with appropriate quantitative dilution (using cylinders containing ten to several hundred milligrams of SO<sub>2</sub> per cubic metre of air).

Gas cylinders containing SO<sub>2</sub> standards shall be made of an inert material or have been passivated to ensure concentration stability of  $\pm 3\%$  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<sub>2</sub>, 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.