SLOVENSKI STANDARD
SIST ISO 6767:1996

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Zunanji zrak - Določanje masne koncentracije žveplovega dioksida - (TCM) Tetrakloromerkuratna/pararosanilinska metoda

Ambient air - Determination of the mass concentration of sulfur dioxide - Tetrachloromercurate (TCM)/pararosaniline method

Air ambiant - Détermination de la concentration en masse du dioxyde de soufre - Méthode au tétrachloromercurate (TCM) et à la pararosaniline

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INTERNATIONAL STANDARD

ISO 6767

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

Air ambiant — Détermination de la concentration en masse du dioxyde de soufre — Méthode au tétrachloromercurate (TCM) et à la pararosaniline

Reference number
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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.

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.

International Standard ISO 6767 was prepared by Technical Committee ISO/TC 146, *Air quality*.

Annexes A and B form an integral part of this International Standard. Annex C is for information only.

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Introduction

This International Standard is a guideline, based on the West-Gaeke method, for the determination of the mass concentration of sulfur dioxide in ambient air. In annex A, a test is given for the purity and purification of pararosaniline hydrochloride; in annex B, a determination is given for the mass concentration of sulfur dioxide present in the sodium disulfite solution used for routine checks; in annex C, a method is given for the recovery of mercury from fresh and used solutions.

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

1 Scope

This International Standard specifies a spectrophotometric method, known as the tetrachloromercurate (TCM)/pararosaniline method, for the determination of the mass concentration of sulfur dioxide in ambient air within the range of 20 µg/m^3 to about 500 µg/m^3.

The sampling period is 30 min to 60 min.

If a longer sampling period than 60 min is used, or higher concentrations of sulfur dioxide (up to about 2 000 µg/m^3) are expected, care is necessary to ensure that the concentrations of sulfur dioxide in the absorption solution given in clause 6, paragraph 2 are not exceeded. This can be achieved by a reduction of the volume flow rate during sampling. Sample solutions obtained by this procedure may be stored for up to 24 h before making measurements, provided that they are kept in a refrigerator at about 5 °C.

Substances which are known to interfere and which might be present in the air being sampled are listed in 7.5

Indications of the precision and accuracy of the method, and of the lower detection limit are given in 8.2.

Detection limit, standard deviations and interferences qualify the TCM-method for orientating field measurements in the higher concentration range. When more accurate measurements are necessary, instruments which are specially tested and calibrated should be used.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 4219:1979, *Air quality — Determination of gaseous sulphur compounds in ambient air — Sampling equipment.*

ISO 6349:1979, *Gas analysis — Preparation of calibration gas mixtures — Permeation method.*

3 Principle

Absorption of sulfur dioxide present in the air sample by passage through a sodium tetrachloromercurate (TCM) solution within a specified period resulting in the formation of a dichlorosulfitomercurate complex.

Destruction of any nitrite ions formed in the sodium tetrachloromercurate solution, by nitrogen oxides present in the air sample, by adding sulfamic acid solution. Conversion of the dichlorosulfitomercurate complex into intensely violet coloured pararosaniline methyl sulfonic acid, by adding a formaldehyde solution and an acidified pararosaniline hydrochloride solution to the resultant solution.

Determination of the absorbance of the sample solution at a wavelength of about 550 nm using an appropriate spectrophotometer (or colorimeter) and calculation of the mass concentration of sulfur dioxide by means of a calibration graph prepared using calibration gas mixtures.

Depending on the the equipment available in the laboratory, it may be convenient to use sodium disulfite solutions for routine checks. However, the solutions are only used after proper calibration using a permeation device.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water, preferably double-distilled water, or water of equivalent purity, free from oxidants.

WARNING — Use the reagents in accordance with the appropriate health and safety regulations.

4.1 Sodium tetrachloromercurate (TCM), absorption solution, $c(Na_2[HgCl_4]) = 0{,}04$ mol/l.

Dissolve 10,9 g of mercury(II) chloride ($HgCl_2$), 4,7 g of sodium chloride (NaCl) and 0,07 g of ethylenedinitrilo tetraacetic acid, disodium salt dihydrate $[(HOCOCH_2)_2N(CH_2)_2N(CH_2COONa)_2.2H_2O]$ EDTA in water in a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix well.

Store the solution in a well stoppered bottle.

The solution is stable for several months, but discard it if a precipitate is formed.

NOTE 1 A procedure for recovering mercury from fresh and used solutions is given in annex C.

4.2 Pararosaniline hydrochloride (PRA), 0,16 g/l solution.

4.2.1 Transfer 86 ml of approximately 38 % (*m*/*m*) hydrochloric acid (HCl) ($\rho \approx 1{,}19$ g/ml) into a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix well.

4.2.2 Transfer 205 ml of approximately 85 % (*m*/*m*) phosphoric acid H_3PO_4 ($\rho \approx 1{,}69$ g/ml) into a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix well.

4.2.3 Dissolve 0,2 g of pararosaniline hydrochloride ($C_{19}H_{17}N_3.HCl$), the purity of which has been tested for each new PRA batch according to annex A, in 100 ml of the hydrochloric acid solution prepared in 4.2.1 .

4.2.4 Pipette 20 ml of the solution prepared in 4.2.3 into a 250 ml one-mark volumetric flask. Add 25 ml of the phosphoric acid solution prepared in 4.2.2. Mix well, and make up to the mark with water.

The solution is stable for several months if stored in the dark.

If the PRA solution is prepared from a PRA stock solution obtained by the purification of PRA in accordance with clause A.2, for each 1 % of difference between a degree of purity of 100 % and the degree of purity obtained, add an additional 0,2 ml of PRA stock solution before making up to the mark with water.

4.3 Formaldehyde, approximately 2 g/l solution.

Pipette 5 ml of a commercially available 36 % (*m*/*m*) to 38 % (*m*/*m*) formaldehyde (HCHO) solution into a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix well.

Prepare this solution on the day of use.

4.4 Sulfamic acid, 6 g/l solution.

Dissolve 0,6 g of sulfamic acid (NH_2SO_3H) in 100 ml of water.

This solution is stable for a few days, if protected from air.

4.5 Sodium disulfite, 0,012 g/l solution.

4.5.1 Dissolve 0,3 g of sodium disulfite ($Na_2S_2O_5$) in 500 ml of freshly distilled water which has been deaerated, for example by boiling and cooling to room temperature.

This solution is not stable.

This solution contains the mass equivalent of 320 µg to 400 µg of sulfur dioxide per millilitre. Determine, as specified in annex B, the actual mass concentration of sulfur dioxide present in the solution.

4.5.2 Immediately after the determination of the actual mass concentration of sulfur dioxide present in the solution as specified in 4.5.1, pipette 2,0 ml of this solution into a 100 ml one-mark volumetric flask. Make up to the mark with absorption solution (4.1) and mix well.

This solution is stable for 30 days, if stored at about 5 °C, or for one day only, if stored at room temperature.

4.6 Calibration gas mixtures.

Immediately before use, prepare zero gas and gas mixtures of sulfur dioxide and air, using the permeation technique specified in ISO 6349. The latter shall be available in at least four different mass concentration levels of sulfur dioxide covering the desired working range.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Sampling equipment, as specified in ISO 4219 and in 5.1.1 to 5.1.5.

5.1.1 Air intake (see ISO 4219), made of polytetrafluoroethylene or borosilicate glass washed with perchloric acid then with distilled water and dried.

5.1.2 Filter for particulate matter (see ISO 4219).

Whenever possible, avoid the use of a filter for particulate matter. However, if a filter for particulate matter is used it shall be made of a material which meets the requirements specified in ISO 4219.

5.1.3 Absorber (see ISO 4219).

The absorption efficiency of the absorption bottle for sulfur dioxide shall be determined before use and shall be at least 0,95. Examples of suitable absorption bottles are given in figure 1.

The absorption efficiency varies with the geometry of the bottle, the size of the gas bubbles and their contact time with the solution. It can be determined by inserting into the sampling train a second absorber in series with the first, and relating the amount of sulfur dioxide found in the first bottle to the total amount of sulfur dioxide found in the two absorbers. When working with midget impingers under the conditions described in clause 6, the absorption efficiency was found to be better than 0,98.

The use of mixtures of sulfur dioxide and air for calibration, as described in 7.1, automatically takes into account the absorption efficiency of the system.

5.1.4 Gas meter or air-flow regulator (see ISO 4219).

As an alternative to the gas meter, a critical orifice in a temperature controlled box can be used. In this case, the pump shall be able to reach $p_d/p_u \leqslant 0,5$, where p_d and p_u are the pressures downstream and upstream of the needle, respectively (see 5.1.5).

5.1.5 Two manometers, accurate to 1 kPa, for measurement of pressure when using a critical orifice instead of a gas meter.

5.2 Spectrophotometer or **colorimeter**, suitable for measuring the absorbance at about 550 nm. If a spectrophotometer is used, carry out the measurements with the instrument set at a wavelength of 548 nm. If a colorimeter is used, use a filter that has its transmittance maximum at a wavelength between 540 nm and 550 nm. Reagent blank problems may occur with apparatus having a spectral bandwith greater than 20 nm.

5.3 Optical cells, plane matched pairs, with an optical path length of 1,0 cm to 5,0 cm.

5.4 Polyethylene bottle, of capacity 100 ml, for transferring the exposed absorption solutions to the laboratory.

6 Sampling

Assemble a sampling train in accordance with the examples shown in figure 2 and any special requirements for the air mass under investigation.

Transfer 10 ml of the aborption solution (4.1) to an absorption bottle (5.1.3) and insert it into the sampling train. Choose a sampling period of either 30 min or 60 min and a volume flow rate between 0,5 l/min and 1 l/min.

The best results are obtained if 0,25 µg to 2,5 µg (0,1 µl to 0,95 µl at 25 °C and 101,3 kPa) of sulfur dioxide per millilitre of absorption solution is trapped.

After sampling, determine the volume of air sampled and note the atmospheric pressure (see 8.1, note 3). If the laboratory sample has to be stored before analysis, it may be kept at 5 °C for not longer than 24 h.

If the laboratory sample shows a precipitate, it is probably due to the reaction of mercury(II) with a reducing sulfur compound. Remove the precipitate by filtration or centrifugation before the analysis.

7 Procedure

7.1 Calibration

7.1.1 Preparation of a set of calibration solutions

Mixtures of sulfur dioxide and air are prepared according to ISO 6349.

In order to prepare the calibration graph, which is a plot of absorbance versus sulfur dioxide concentration, at least four different concentration levels of sulfur dioxide within the range specified in clause 2 are needed.

Sample each gas mixture under the same conditions as are used for the unknown air sample, in particular for the same sampling period and at the same flow rate. Treat the obtained sample solutions as described in 7.3 (see 4.6).

7.1.2 Zero member solution

Prepare a zero member solution from zero gas (see 4.6). This preparation is carried out according to 7.1.1.