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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*



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Foreword

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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.

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 $\mu\text{g}/\text{m}^3$ to about 500 $\mu\text{g}/\text{m}^3$.

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 $\mu\text{g}/\text{m}^3$) 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, $c(\text{Na}_2[\text{HgCl}_4]) = 0,04 \text{ mol/l}$.

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 $[(\text{HOCOCH}_2)_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2\text{COONa})_2 \cdot 2\text{H}_2\text{O}]$ 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) ($\rho \approx 1,19 \text{ g/ml}$) 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 ($\rho \approx 1,69 \text{ g/ml}$) 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 ($\text{C}_{19}\text{H}_{17}\text{N}_3 \cdot \text{HCl}$), 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 ($\text{NH}_2\text{SO}_3\text{H}$) 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 ($\text{Na}_2\text{S}_2\text{O}_5$) in 500 ml of freshly distilled water which has been de-aerated, 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