BRITISH STANDARD

BS 1747-7:
1983
ISO 4221:1980

Methods for

Measurement of air pollution —

Part 7: Determination of mass concentration of sulphur dioxide in ambient air: Thorin spectrophotometric method

[ISO title: Air quality — Determination of mass concentration of sulphur dioxide in ambient air: Thorin spectrophotometric method]

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This British Standard, having been prepared under the direction of the Environment and Pollution Standards Committee, was published under the authority of the Board of BSI and comes into effect on 31 January 1983

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The following BSI references relate to the work on this standard:
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Amd. No.	Date of issue	Comments

Contents

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National foreword

This Part of this British Standard, which has been prepared under the direction of the Environment and Pollution Standards Committee, is identical with ISO 4221:1980 "*Air quality — Determination of mass concentration of sulphur dioxide in ambient air — Thorin spectrophotometric method*".
The International Standard was prepared by Technical Committee 146, Air quality, and published by the International Organization for Standardization (ISO) as a result of discussion in which the UK participated.

This Part of this British Standard is one of a series relating to air quality arising from the UK participation in the work of ISO/TC 146. Methods for the determination of particular constituents of ambient air will be published as further Parts of this standard. Topics relating to air quality characteristics will be published as Parts of BS 6069 "*Methods for characterization of air quality*".

Terminology and conventions. The text of the International Standard has been approved as suitable for publication as a British Standard without deviation. Some terminology and certain conventions are not identical with those used in British Standards; attention is especially drawn to the following.

The comma has been used throughout as a decimal marker. It is current practice in British Standards to use a full point on the baseline as the decimal marker.

Wherever the words "International Standard" appear, referring to this standard, they should be read as "British Standard".

Cross-reference

International Standard	Corresponding British Standard
ISO 4219:1979	BS 1747 *Methods for measurement of air pollution* Part 6:1982 *Sampling equipment used for the determination of gaseous sulphur compounds in ambient air* (Identical)

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 8, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

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1 Scope

This International Standard specifies a Thorin[1] spectrophotometic method for the determination of the mass concentration of sulphur dioxide in ambient air.

2 Field of application

This method is applicable to the determination of the mass concentration of sulphur dioxide in ambient air within the range of 3,5 to 150 µg/m^3, assuming an air sample volume of 2 m^3 and a sample solution volume of 50 ml. For higher concentrations, dilution of the sample may be necessary before carrying out the determination.[2]

Interference from ammonia and hydrogen sulphide may occur if these are present in very high concentrations. Interferences from particulate matter are avoided at the sampling stage by filtering the air. (See also **8.3**.)

NOTE Diluting may be sometimes unnecessary if the air sample collected over a specified period is reduced by dividing the overall sampling period into intervals of the same duration and sampling in such a way that intervals of absorption are followed by intervals where the sampling pump is switched off.

3 Reference

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

4 Principle

Absorption and oxidation of the sulphur dioxide present in the sampled air by drawing the sample for a specified period through an acidified solution of hydrogen peroxide of defined pH, resulting in the formation of sulphuric acid.

Precipitation of the sulphate ions formed as barium sulphate by reaction with excess barium perchlorate and determination of residual barium ions by complexing with Thorin and measurement of the coloured complex spectrophotometrically at 520 nm.

NOTE The difference between the initial and final quantity of barium ions corresponds to the concentration of sulphate ions in the absorption solution, and thus to the amount of sulphur dioxide that has been oxidized. The absorbance varies inversely with the concentration of sulphate ions present in the absorption solution.

5 Reagents

During the analysis, use only reagents of recognized analytical grade and only double-distilled or de-ionized and distilled water.

WARNING — Handle carefully the following hazardous substances: perchloric acid solution, barium perchlorate solution, dioxane and Thorin.

5.1 *Hydrogen peroxide,* 27 to 30 % (*m*/*m*) solution.

5.2 *Absorption solution*

Dilute 10 ml of the hydrogen peroxide solution (**5.1**) to 1 000 ml with water. Adjust the pH of the solution to between 4,0 and 4,5 with the perchloric acid solution (**5.4**), preferably using a pH meter.

Store this solution in a refrigerator and discard after 1 month.

5.3 *Perchloric acid,* 0,1 mol/l solution.

Add 4,3 ml of a 72 % (*m*/*m*) solution of perchloric acid ($HClO_4$) to water in a 500 ml one-mark volumetric flask. Dilute to the mark and mix.

5.4 *Perchloric acid,* approximately 0,01 mol/l solution.

Prepare from the 0,1 mol/l solution (**5.3**).

5.5 *Barium perchlorate* solution.

Dissolve 0,525 g of anhydrous barium perchlorate [$Ba(ClO_4)_2$] in a small quantity of the perchloric acid solution (**5.3**) in a 250 ml one-mark volumetric flask. Dilute to the mark with the same perchloric acid solution and mix.

5.6 *Barium perchlorate/dioxane solution*

Add 10 ml of the barium perchlorate solution (**5.5**) to 40 ml of water in a 1 000 ml one-mark volumetric flask. Dilute to the mark with dioxane and mix.

NOTE 1 Several organic solvents may be used, for example dioxane, *iso*propanol, acetone. The most favourable calibration curve, however, is obtained with dioxane.

NOTE 2 The organic solvent is chosen to minimize the solubility product of the barium sulphate, but because this is still significant in the lower region of the concentration range, a small constant amount of sulphate ion is added to the blank solution, the standard matching solutions and the aliquot portion of the exposed sample.

5.7 *Thorin,* 2,5 g/l solution.

Dissolve 0,125 g of Thorin in 20 ml of the standard sulphate solution (**5.8.2**) and a small quantity of water in a 50 ml one-mark volumetric flask. Dilute to the mark with water and mix.

Prepare this solution daily.

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[1] Thorin is also known as Thoron or Thoronol, the sodium salt of 4-[(2-arsonophenyl) azo]3-hydroxy 2,7-naphthalene-disulphonic acid.

[2] An International Standard specifying a tetrachloromercurate (TCM)/pararosaniline spectrophotometric method for the determination of the mass concentration of sulphur dioxide in ambient air is in preparation, and should be used when greater sensitivity is required.

5.8 *Standard sulphate solutions*

5.8.1 *Sulphate,* standard solution containing 0,5 mol of sulphuric acid (H_2SO_4) per litre.

Standardize this solution accurately by titration against a standard volumetric sodium hydroxide solution, which has been standardized itself against potassium hydrogen phthalate ($KHC_8H_4O_4$).

1 ml of this standard solution corresponds to 32 mg of SO_2.

5.8.2 *Sulphate,* standard solution containing 0,001 25 mol of sulphuric acid (H_2SO_4) per litre.

Prepare from the standard sulphate solution (**5.8.1**) by diluting as follows:

a) Measure by pipette 25 ml of the standard sulphate solution into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this standard solution corresponds to about 800 µg of SO_2.

b) Measure by pipette 10 ml of the standard sulphate solution obtained in a) into a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this standard solution corresponds to about 80 µg of SO_2.

6 Apparatus

Ordinary laboratory apparatus and

6.1 *Sampling equipment* as specified in ISO 4219, subclauses **5.1** to **5.7** and, in addition, as specified in **6.1.1**.

6.1.1 *Absorption bottles*

Borosilicate glass bottles of the Drechsel type equipped with interchangeable ground glass joints (see Figure 1) shall be used. A bottle having the cone of the ground glass joint on the bottle is preferable, because of the smaller risk of deposited matter dropping into the absorption solution when the sampling head is removed.

The capacity of the bottle shall be 125 ml for 24 h sampling and 250 ml for 48 h sampling. The external diameter of the entry and exit tubes of the absorption bottle shall be 10 mm to 12 mm. The tube leading the air into the solution shall have an internal diameter of 6 to 8 mm and shall end 5 to 10 mm from the bottom of the bottle.

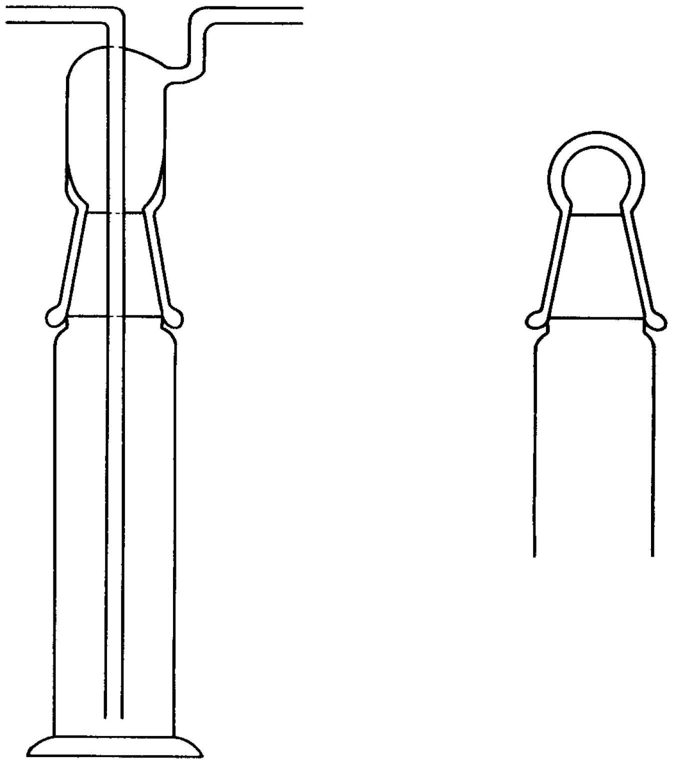

Figure 1 — Absorption bottle (The dimensional proportions are approximate.)

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6.2 *Spectrophotometer, single-or double-beam type*

If a single-beam spectrophotometer is to be used, it shall be possible to adjust the incident light intensity, for example, by adjusting a diaphragm or by slit-width control. For a single-beam spectrophotometer, the greatest accuracy is achieved if the incident light beam intensity can be adjusted to give a "read absorbance" value as close to 0 as possible for the highest measurable concentration. However, with the instruments currently available, the best possible result is obtained if the adjusted light intensity results in a "read absorbance" value of 0,800 for the blank solution in a 10 mm or 20 mm cell. Using a double-beam instrument, the difference in the absorbance between the sample (or the standard solutions) and the blank can be read directly.

NOTE **read absorbance value:** The reading value on the face of a single-beam spectrophotometer; the measured signal is proportional to the logarithm of the intensity.

6.3 *Glass cells,* having an optical path length of 10 or 20 mm.

If more than one cell is used, the cells shall be matched photometrically.

6.4 *Pipettes,* of capacity 0,25 ml, or *dispensing and diluting apparatus.*

7 Sampling

Set up the equipment specified in ISO 4219 in accordance with the requirements of ISO 4219 and any special requirements for the atmosphere to be sampled (see **8.3**).

Insert a particulate filter (**5.3** of ISO 4219) into the filter holder (**5.3.2** of ISO 4219).

In one of the absorption bottles (**6.1.1**) place a suitable quantity of the absorption solution (**5.2**), mark the level of the solution and connect the bottle to the sample train.

For a sampling period of 24 h, the volume used shall be 50 ml and for a sampling period of 48 h 150 ml.

NOTE 1 If the temperature of the air sampled exceeds 25 °C or if the air is very dry, larger volumes of absorption solution may have to be used. The correct amount needed to absorb all the sulphur dioxides in the test sample collected during the selected test duration should be ascertained by preliminary tests.

NOTE 1 Automatic equipment for changing the absorption bottles may be used.

Adjust the flow regulator (**5.6** of ISO 4219) to give a flow rate of 90 l/h. Record the reading on the gas meter (**5.6** of ISO 4219) and the time and start the sampling pump (**5.7** of ISO 4219).

At the end of the sampling period, switch off the sampling pump, note the reading on the gas meter and the time. Remove the absorption bottle from the sampling train and make up the level to the original level with water.

In order to avoid the possible contamination of the aliquot portions to be analysed, either stopper the bottle tightly or, if this is not possible, transfer the contents to a clean, dry transfer bottle and send it to the laboratory for analysis.

Replace the bottle removed by a second bottle containing fresh absorption solution and renew the particulate filter.

8 Procedure

8.1 Preparation of calibration curve

8.1.1 ***Standard matching solutions***

Prepare a series of standard matching solutions having sulphate concentrations corresponding to sulphur dioxide concentrations of 0,8 – 1,6 – . . . – 8,0 µg/ml by placing portions of 1,00 – 2,00 – . . . – 10,00 ml respectively of the standard sulphate solution (**5.8.2**) into a series of 100 ml one-mark volumetric flasks, diluting to the mark and mixing.

8.1.2 ***Blank test solution***

Prepare a blank test solution by mixing thoroughly 4,0 ml of water, 10 ml of the barium perchlorate/dioxane solution (**5.6**) and 0,25 ml of the Thorin solution (**5.7**) in the best reproducible way, using either the pipettes or the dispensing and diluting apparatus (**6.4**).

Add the Thorin solution just before measuring the absorbance of the solution. Note that the blank solution is stable for 30 min if left in the dark.

8.1.3 ***Standard test solutions***

Prepare a series of test solutions corresponding to each of the standard matching solutions (**8.1.1**) by mixing 4,0 ml of each with the same quantities of reagents as for the blank solution (**8.1.2**).

Measure the absorbance of the test solutions within 10 min.

8.1.4 ***Measurement***

Check the spectrophotometer (**6.2**) in accordance with the manufacturer's instructions and after stabilization, adjust the wavelength to 520 nm.[3]

To obtain a reliable result, it is advisable to carry out the measurement with the same solution two or three times at least.

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[3] The adjustment of the spectrophotometer shall be checked frequently with freshly prepared blank test solution.

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8.1.4.1 *Single-beam instruments*

Fill a cell (**6.3**) with the blank test solution (**8.1.2**), place it in the light path and adjust the absorbance reading to 0,800.[3] Replace the blank test solution with each of the standard test solutions in turn and measure the absorbance of each solution.

8.1.4.2 *Double-beam instruments*

Fill two cells with the blank test solution (**8.1.2**), place these into the reference and measuring light paths and adjust the absorbance difference to zero. Replace the blank test solution in the cell in the reference light path by each of the standard test solutions in turn and measure the absorbance difference for each solution.

8.1.5 *Calibration curve*[4]

Prepare a calibration curve by plotting the absorbance of each standard test solution, including the blank (single-beam instruments), against either the concentration of sulphur dioxide in the corresponding standard matching solution (**8.1.1**) or the absorbance difference from the blank test (double-beam instruments) (see Figure 2 to Figure 5).

8.2 Determination

Adjust the temperature of the absorption solution containing the test sample obtained according to clause **7** to the same as that of the reagent solutions.

To ensure the result, it is necessary to determine the concentration of sulphur dioxide in the sample solution on at least two or three test portions.

8.2.1 *Test portion*

Take by pipette 4,0 ml of the solution in the absorption bottle.

8.2.2 *Test solution*

Mix the test portion (**8.2.1**) with 10 ml of the barium perchlorate/dioxane solution (**5.6**) and 0,25 ml of the Thorin solution (**5.7**) as specified in **8.1.2**.

8.2.3 *Measurement*

Fill a cell with the test solution (**8.2.2**) and measure its absorbance as specified in **8.1.4** within 10 min. Determine the concentration of sulphur dioxide in the test portion by reference to the appropriate calibration curve (**8.1.5**). For good accuracy, only the linear part of the calibration curve, i.e. between 0 and 6 µg/ml sulphur dioxide concentration, should be used.

If the concentration of sulphur dioxide in the sample exceeds 6 µg/ml, take a new aliquot portion of the absorption solution and dilute with water to a suitable volume. Note the dilution factor *f* and proceed according to **8.2.1**, **8.2.2** and **8.2.3** above.

8.3 Interferences

Thorin forms complexes with many metallic cations, but the use of the particulate filter at the sampling stage should ensure that none are present in the sample. The use of a filter also removes phosphate, which would interfere by precipitating barium as barium phosphate.

Very high concentrations of ammonia and hydrogen sulphide may interfere; the former may move the pH of the sample solution outside the limits required for the analysis, the latter may be oxidized to sulphuric acid in the absorption bottle. If the pH of the absorption solution falls below 3,5 or exceeds 9,8, the evaluation of the concentration of sulphur dioxide obtained will be too high or too low respectively. The pH of the absorption solution to be analysed may vary between 3,5 and 9,8 without interference.

9 Expression of results

9.1 Method of calculation

The mass concentration of sulphur dioxide (SO_2) in the air sample is given, in micrograms per cubic metre, by the formula

$$\varrho\,(SO_2) = f \times \varrho_{cal} \times \frac{V_1}{V_2}$$

where

f is the dilution factor (see **8.2.3**);

ϱ_{cal} is the mass concentration of sulphur dioxide, in micrograms per millilitre, read from the calibration curve;

V_1 is the initial volume, in millilitres, of the absorption solution;

V_2 is the volume, in cubic metres, of the air sample.

Express the result as the mean of two or three determinations (see **8.2**).

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[4] A new calibration curve shall be prepared for every fresh batch of Thorin solution and barium perchlorate/dioxane solution used.

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9.2 Detection limit

9.2.1 *Single-beam spectrophotometer*

The absorbance of the blank solution (absorbance reading 0,800) may be determined within ± 0,003, which is the noise level of the spectrophotometer. The detection limit is set for a signal three times stronger than the noise level, i.e. the absorbance value $0,800 - 3 \times 0,003 = 0,791$, corresponding to a concentration of sulphur dioxide of 0,13 µg/ml.

9.2.2 *Double-beam spectrophotometer*

The detection limit is of the same order of magnitude as for the single-beam spectrophotometer, i.e. 0,1 µg/ml.

9.3 Repeatability

9.3.1 *Single-beam spectrophotometer*

The repeatability in terms of standard deviation (sample size $n = 10$) is as follows :

— Using a manual pipette: ± 0,07 µg/ml

— Using a dispensing and diluting apparatus: ± 0,03 µg/ml

9.3.2 *Double-beam spectrophotometer*

Measurements using cation-exchanged potassium sulphate solutions as standards covering the range equivalent to a concentration of sulphur dioxide of between 0,3 µg/ml and 8 µg/ml, show that the overall standard deviation is ± 0,06 µg/ml.

10 Test report

The test report shall include the following particulars :

a) complete identification of the sample;

b) reference to this International Standard;

c) reference to ISO 4219;

d) the results and the method of expression used;

e) any unusual features noted during the determination;

f) any operation not specified in this International Standard or in the International Standard to which reference is made, or regarded as optional.

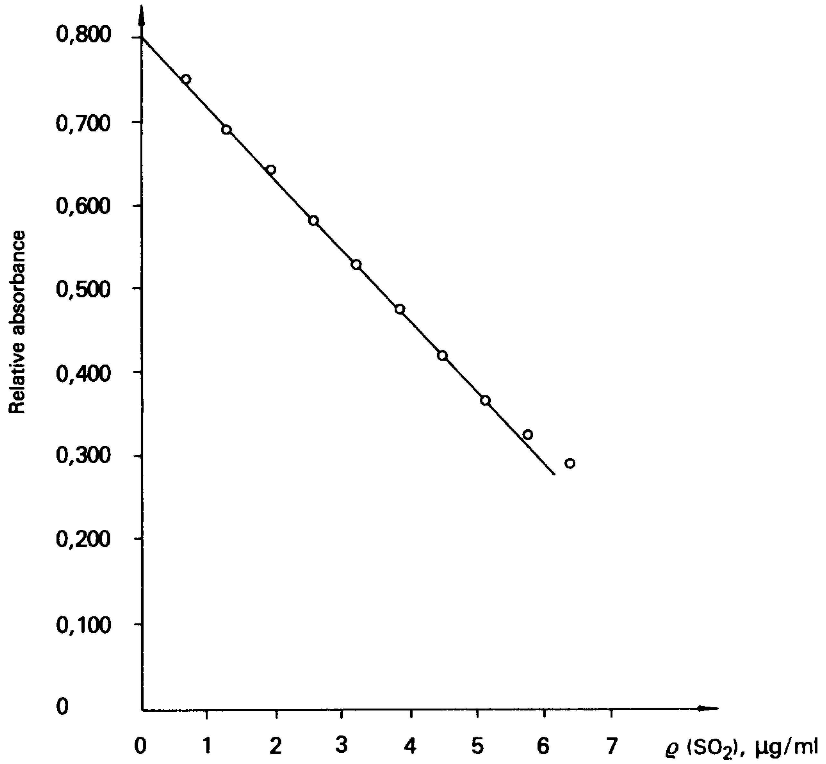

Figure 2 — Typical calibration curve obtained using a single-beam spectrophotometer with cells having an optical path length of 20 mm

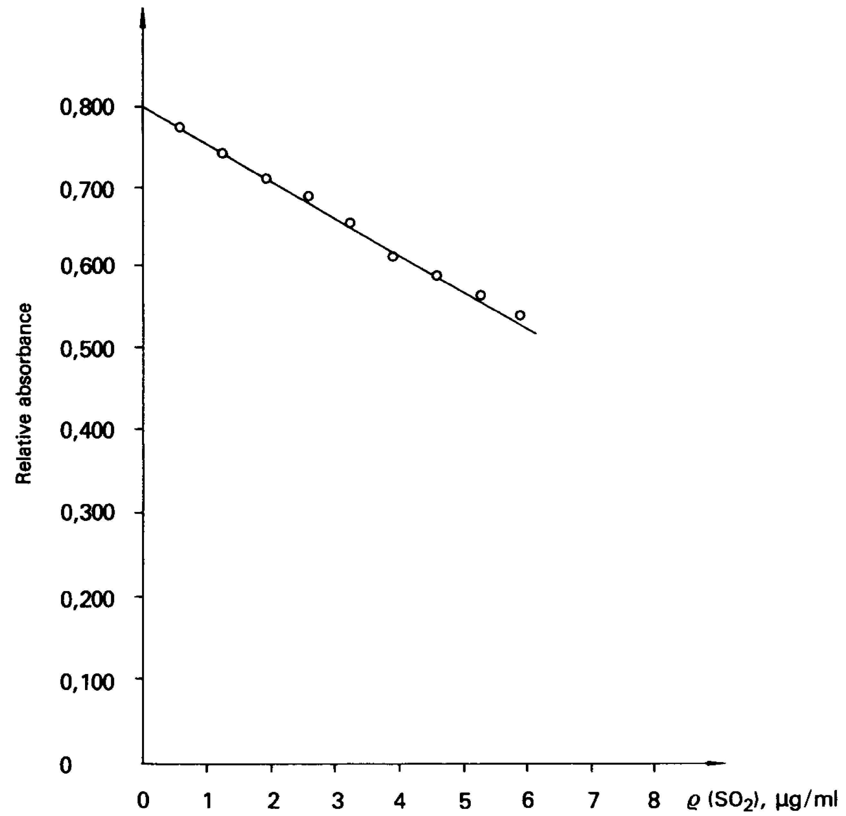

Figure 3 — Typical calibration curve obtained using a single-beam spectrophotometer with cells having an optical path length of 10 mm

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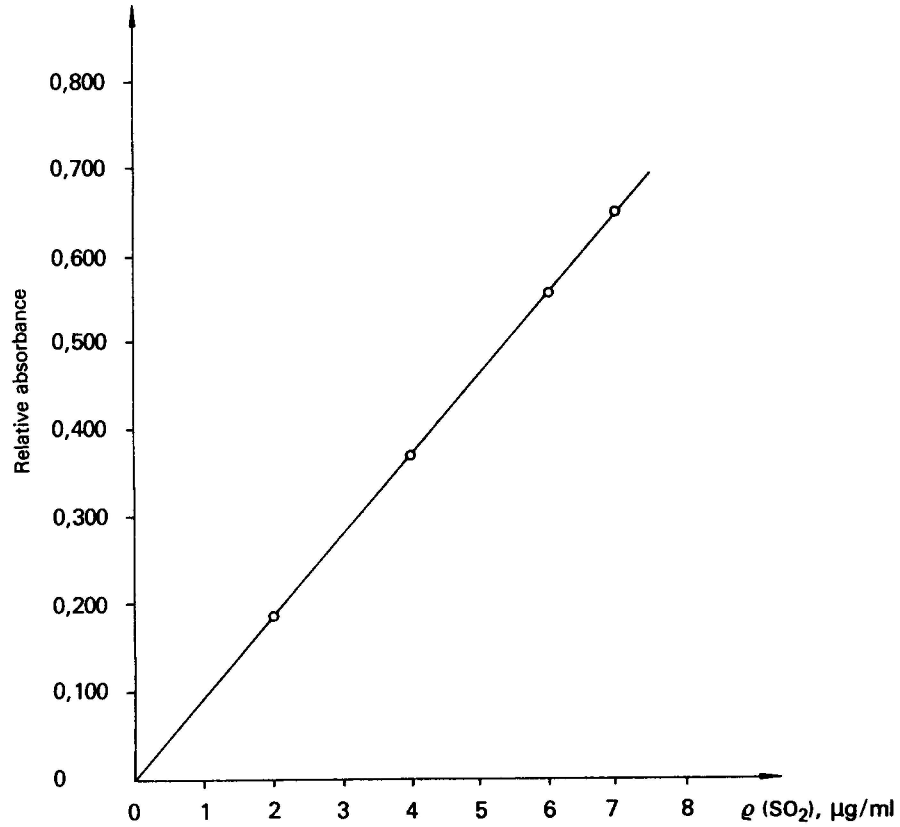

Figure 4 — Typical calibration curve obtained using a double-beam spectrophotometer with cells having an optical path length of 20 mm

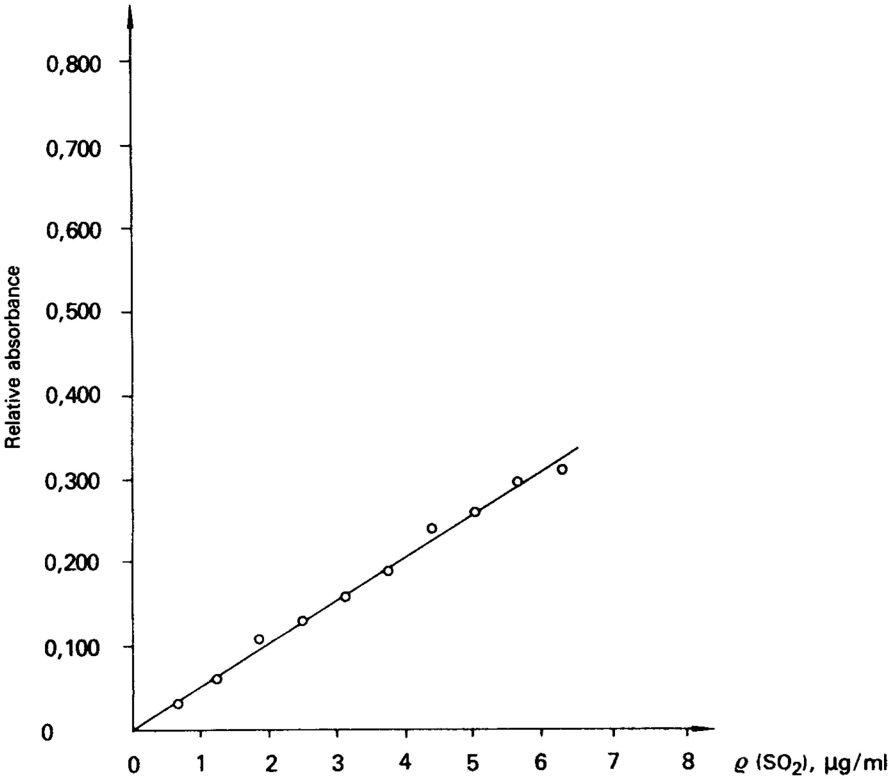

Figure 5 — Typical calibration curve obtained using a double-beam spectrophotometer with cells having an optical path length of 10 mm

Publications referred to

See national foreword.

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