INTERNATIONAL STANDARD

ISO 6326-5

First edition
1989-07-01

Natural gas — Determination of sulfur compounds —

Part 5 :
Lingener combustion method

Gaz naturel — Détermination des composés soufrés —
Partie 5 : Méthode de combustion Lingener

Reference number
ISO 6326-5 : 1989 (E)

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 approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 6326-5 was prepared by Technical Committee ISO/TC 158, *Analysis of gases.*

ISO 6326 consists of the following parts, under the general title *Natural gas — Determination of sulfur compounds*:

- *Part 1: General introduction*
- *Part 2: Gas chromatographic method using an electrochemical detector for the determination of odoriferous sulfur compounds*
- *Part 3: Determination of hydrogen sulfide, mercaptan sulfur and carbonyl sulfide sulfur by potentiometry*
- *Part 4: Determination of individual sulfur compounds by gas chromatography with a flame photometric detector*
- *Part 5: Lingener combustion method*

Annex A of this part of ISO 6326 is for information only.

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Case postale 56 • CH-1211 Genève 20 • Switzerland
Printed in Switzerland

Introduction

The standardization of several methods for the determination of sulfur compounds in natural gas is necessary in view of the diversity of these compounds [hydrogen sulfide, carbonyl sulfide, thiols (mercaptans), tetrahydrothiophene (THT), etc.] and the purposes of the determinations (required accuracy, measurement at the drilling head or in the transmission pipes, etc.).

In order to enable the user to choose the method most appropriate to his needs and to perform the measurements under the best conditions, ISO 6326 has been prepared in several parts.

ISO 6326-1 gives a rapid comparison of standardized methods and therefore provides information for the choice of the method.

The other parts of ISO 6326, including this part, describe in detail the various standardized methods.

The determination of total sulfur is specified in ISO 4260 : 1987, *Petroleum products and hydrocarbons — Determination of sulfur content — Wickbold combustion method.*

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Natural gas — Determination of sulfur compounds —

Part 5 :
Lingener combustion method

1 Scope

This part of ISO 6326 specifies a method for the determination of total sulfur in natural gas. The method is applicable to gases with sulfur contents between 0,5 mg/m^3 and 1 000 mg/m^3. With a total sulfur content of more than 0,1 mg sulfur in the absorption solution, visual titration with an indicator can be chosen, whereas for lower contents turbidimetric titration is preferable.

NOTE — In all parts of ISO 6326, 1 m^3 of gas is expressed at normal conditions (0 °C; 101,325 kPa).

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 6326. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 6326 are encouraged to investigate the possibility of applying the most recent editions of the standards listed below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1 : 1984, *Laboratory glassware — Burettes — Part 1 : General requirements.*

ISO 648 : 1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042 : 1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 3585 : 1976, *Glass plant, pipeline and fittings — Properties of borosilicate glass 3.3.*

3 Principle

A measured volume of gas is burnt with air at atmospheric pressure in a glass combustion apparatus. The resulting sulfur oxides are converted into sulfuric acid by absorption in hydrogen peroxide solution. Depending on the sulfur content of the test gas, the sulfate ions in the absorption solution are determined using either visual titration with an indicator or turbidimetric titration.

4 Reagents and materials

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Hydrogen peroxide, 10 % (*m*/*m*) aqueous solution, sulfur-free, as absorbing liquid for the sulfur oxides.

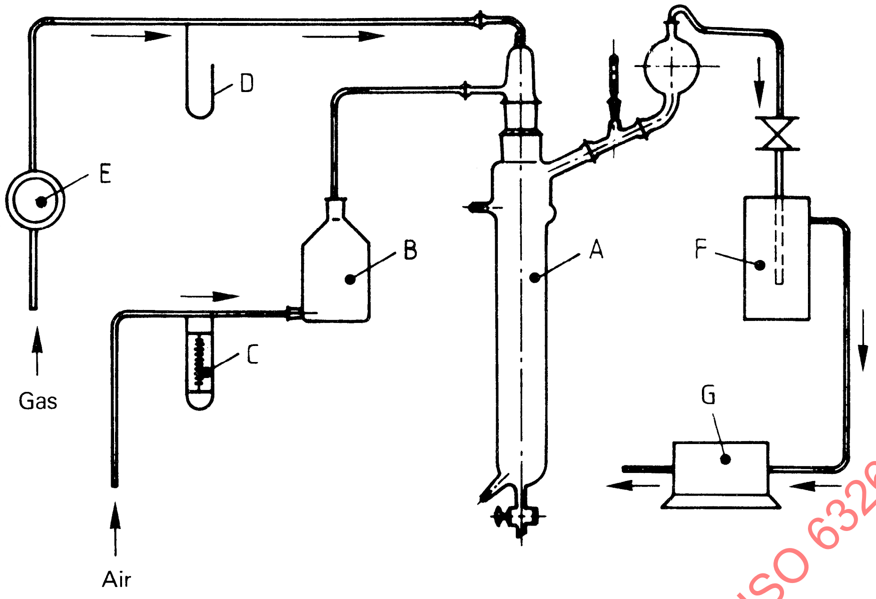
4.2 Activated carbon, for adsorption of sulfur impurities from the combustion air.

4.3 Absorbing liquid : 30 % (*m*/*m*) aqueous solution of potassium hydroxide, for the purification of the combustion air.

5 Apparatus

The schematic layout of the apparatus is shown in figure 1.

Ordinary laboratory apparatus and



A	Combustion device
B	Pressure-equalizing vessel
C	Capillary flow meter
D	U-tube manometer
E	Dry gas meter with thermometer
F	Condensate separator
G	Vacuum pump

Figure 1 — Schematic layout of the apparatus

5.1 Combustion device (A)

The combustion device is manufactured of borosilicate glass complying with ISO 3585. It consists of the parts shown in figure 2.

5.1.1 Receiver with cooling jacket (see figure 3).

5.1.2 Flame tube (see figure 4)

The outer diameter of the flame tube is determined by the inside diameter of the receiver with cooling jacket and the annular gap shown in figure 2.

5.1.3 Burner (see figure 5)

For the combustion of natural gases a universal burner with a needle valve is often preferable.

5.1.4 Intermediate piece (see figure 6)

The thermometer shall have a measuring range of 0 °C to at least 100 °C. The scale interval shall be not less than 1 °C.

5.1.5 Reitmeyer attachment (see figure 7).

5.2 Pressure-equalizing vessel (B).

5.3 Capillary flow meter (C), measuring range 10 l/min to 30 l/min.

5.4 U-tube manometer (D), arm length 500 mm.

5.5 Dry gas meter (E)

The range of the meter shall be appropriate for the quantity of sample to be burned and the meter shall have been recently calibrated. The gas meter shall be equipped with a thermometer for the measurement of the gas temperature. The thermometer shall have a measuring range of 0 °C to at least 30 °C. The scale intervals shall be not less than 0,5 °C.

NOTE — The gas meter should be flushed with the gas to be analysed before the combustion, in particular when analysing gases with different sulfur contents, to avoid disturbance by adsorption and desorption phenomena.

5.6 Condensate separator (F).

5.7 Vacuum pump (G)

The suction capacity of the vacuum pump shall be at least 25 l/min. It is recommended that a drying tower with a drying agent be included between the condensate separator (F) and the vacuum pump (G) to protect the oil in the vacuum pump.

Dimensions in millimetres

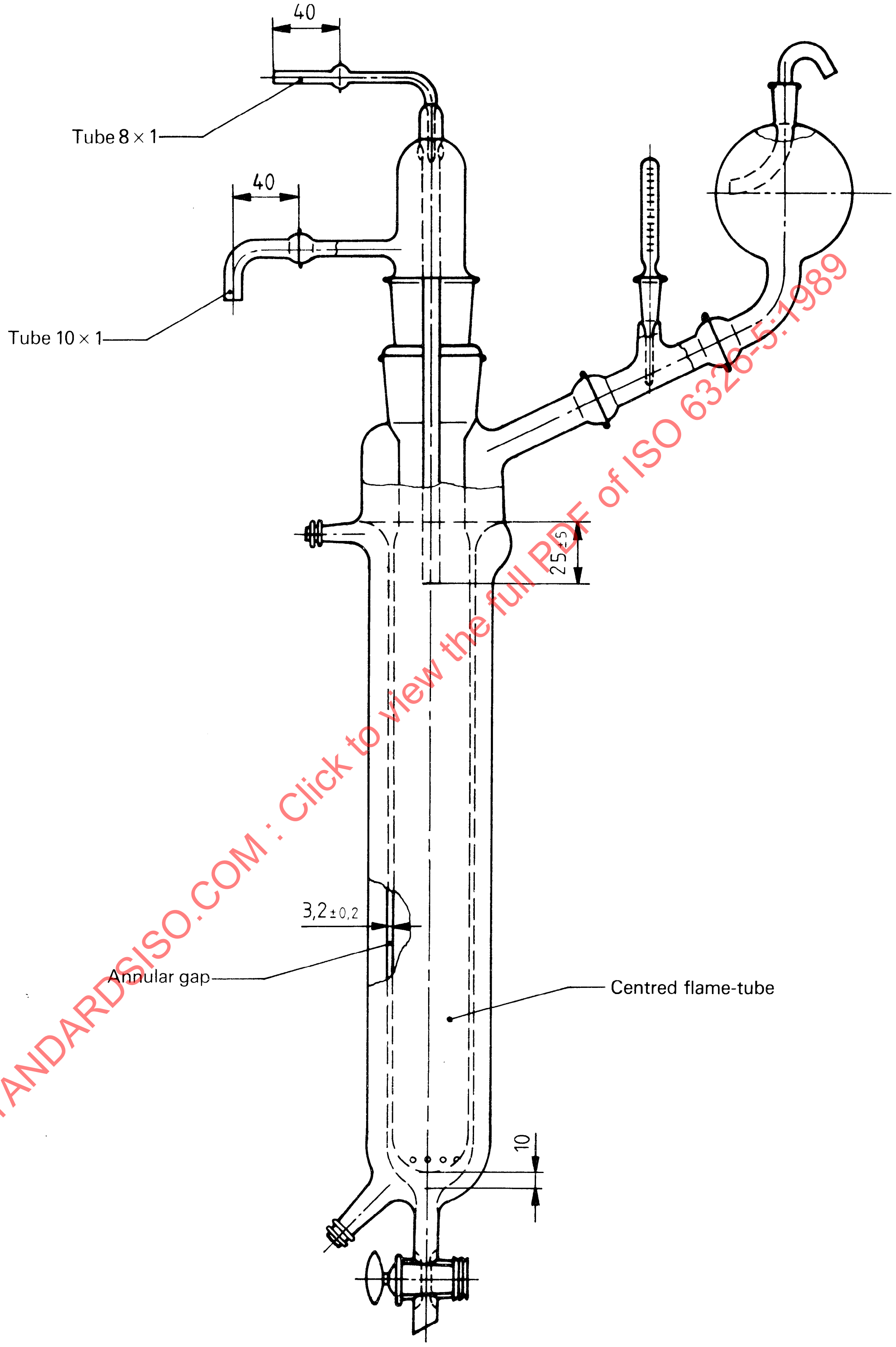


Figure 2 — Combustion vessel

Dimensions in millimetres

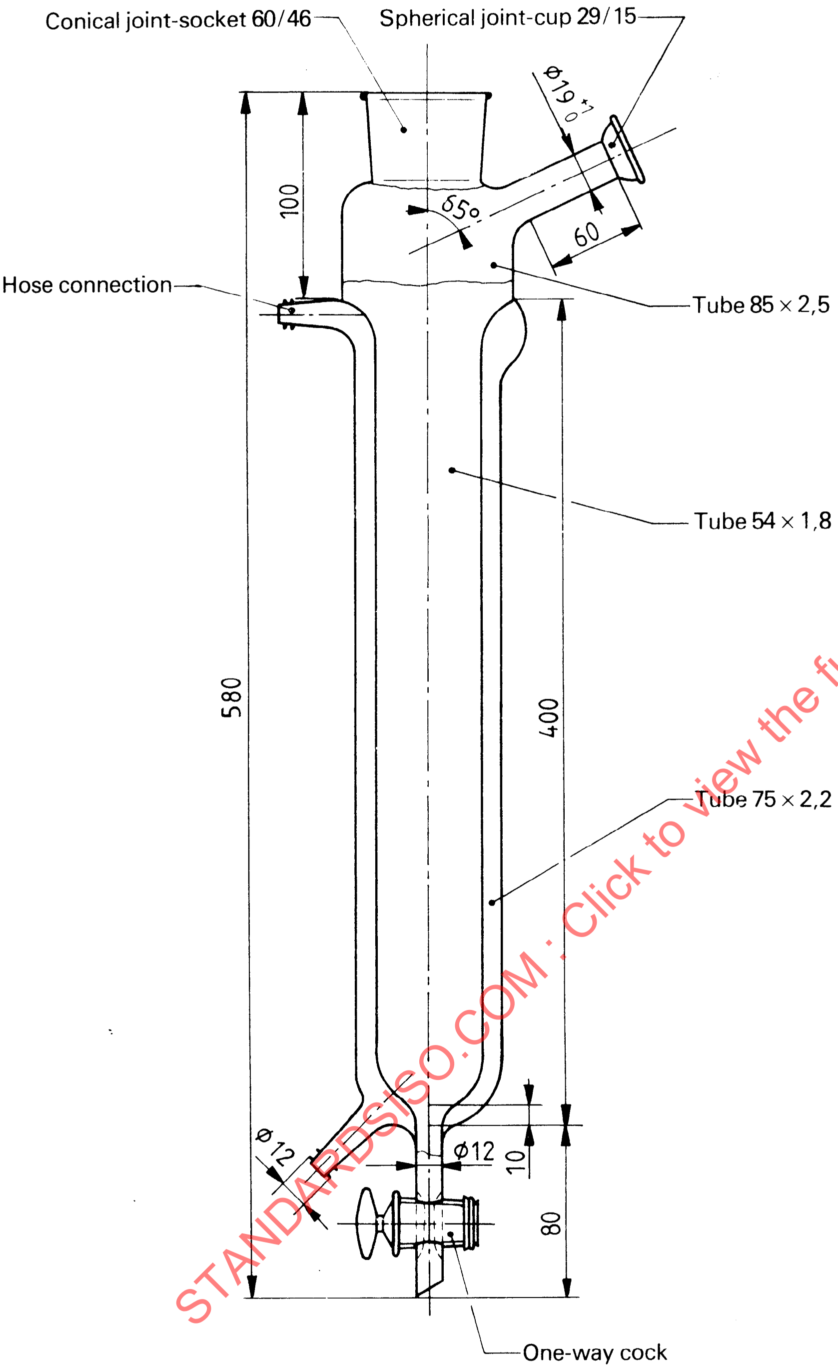


Figure 3 — Receiver with cooling jacket

Dimensions in millimetres

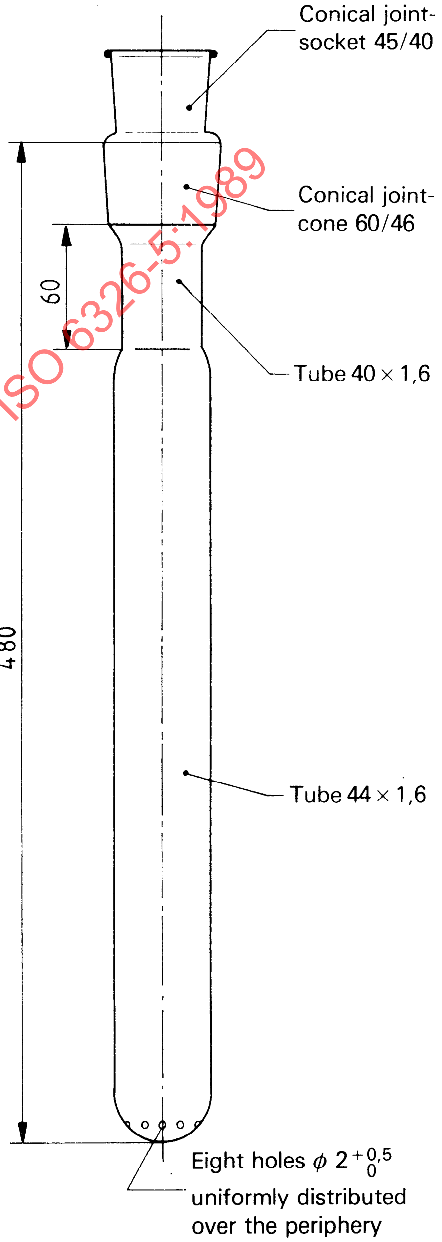


Figure 4 — Flame tube

Dimensions in millimetres

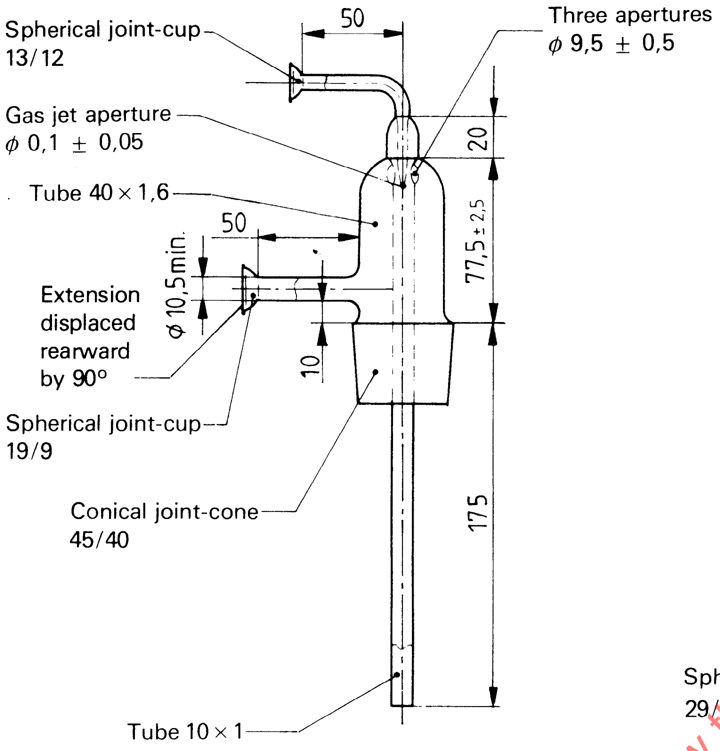


Figure 5 — Burner

Dimensions in millimetres

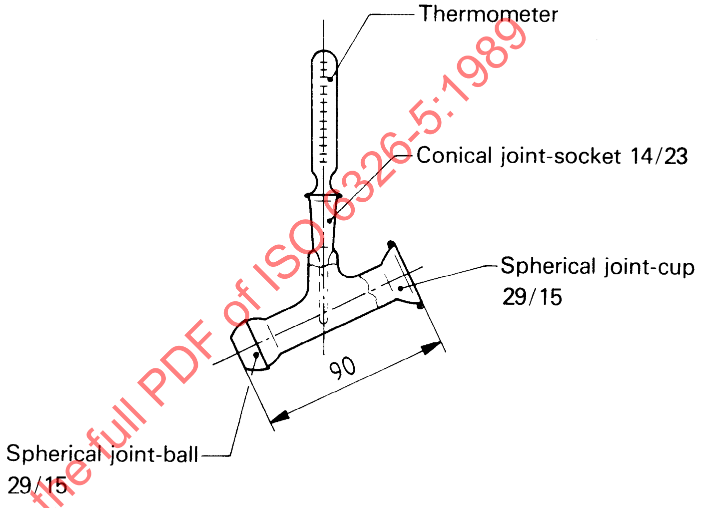


Figure 6 — Intermediate piece

Dimensions in millimetres

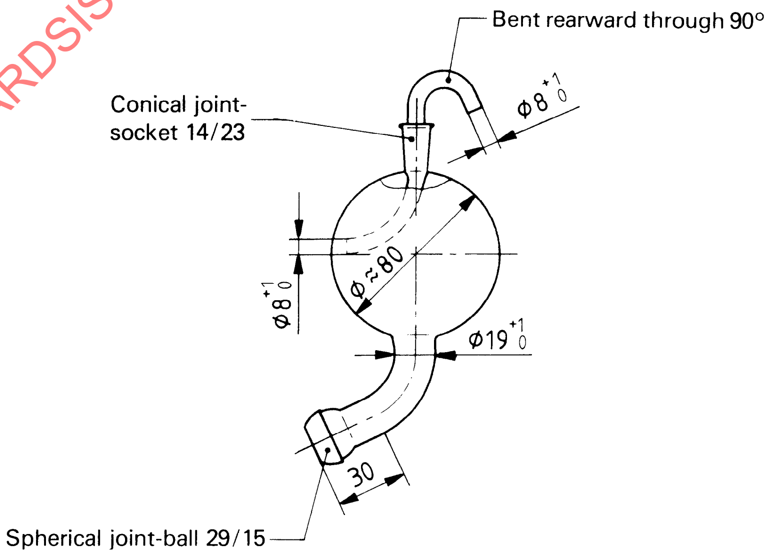


Figure 7 — Reitmeyer attachment

6 Procedure

6.1 Preparation for combustion

Draw air, which if necessary should be cleaned of sulfur impurities with activated carbon (4.2) and/or absorbing liquid (4.3), through the combustion apparatus with the aid of the vacuum pump (G), with a required volumetric flow about 20 l/min. Remove the burner (5.1.3) and pour sufficient hydrogen peroxide solution (4.1) into the receiver (5.1.1) to rise around the flame tube (5.1.2) to the height of the burner tip throughout the period of combustion. After connection of the cooling water, the combustion apparatus is ready for use.

6.2 Combustion

With a preliminary pressure of about 2 kPa on the U-tube manometer (D), ignite the gas at the removed burner. Carefully introduce the burner, with the flame directed downwards, into the flame tube and note the reading on the gas meter (E). The air flow and cooling water flow may have to be adjusted. The temperature and pressure of the gas shall be read during the combustion period. The exhaust gas temperature on the thermometer shall be kept between 50 °C and 70 °C. As soon as the required quantity of gas, up to 500 litres depending on sulfur content (see clause 7) has been burnt, shut off first the gas supply and then the vacuum pump. Drain the absorbing solution into a beaker (7.1.2.5 or 7.2.2.6), rinse the receiver with water and note the reading on the gas meter (E).

6.3 Determination of gas volume

The volume of gas burnt, shown by the difference in readings on the gas meter, shall be reduced to normal conditions:

$$V_n = \frac{V T_n (p_{amb} + p_e)}{p_n T}$$

where

V is the volume of the gas sample measured in accordance with 6.2 at temperature T (kelvins) and pressure $p_{amb} + p_e$ (kilopascals);

T_n is the thermodynamic temperature, in kelvins, at normal ambient conditions (273,15 K);

T is the thermodynamic temperature, in kelvins, of the gas sample;

p_n is the pressure, in kilopascals, at normal conditions (101,325 kPa);

p_{amb} is the atmospheric pressure, in kilopascals, measured during gas sampling;

p_e is the excess pressure, in kilopascals, measured with the water manometer during gas sampling.

7 Analytical determination

With a total sulfur content of more than 0,1 mg sulfur in the absorption solution, visual titration with an indicator can be chosen, whereas for lower contents turbidimetric titration is preferable.

7.1 Determination of sulfur content by visual titration

7.1.1 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

7.1.1.1 2-Propanol (Isopropyl alcohol).

7.1.1.2 Barium perchlorate, standard volumetric solution.

Dissolve 1,7 g of barium perchlorate [$Ba(ClO_4)_2$] in 200 ml of water in the 1 000 ml one-mark volumetric flask (7.1.2.1), make up to the mark with the 2-propanol (7.1.1.1) and adjust to pH 3,5 with perchloric acid. Standardize the solution against a standard reference solution of sulfuric acid, $c(H_2SO_4) = 0{,}005$ mol/l.

1 ml of this standard volumetric solution is equivalent to approximately 0,16 mg of S.

7.1.1.3 Thorin[1], 0,2 % (m/m) aqueous indicator solution.

Store in a silica glass or polyethylene bottle.

7.1.1.4 Methylene blue, 0,01 % (m/m) aqueous indicator solution.

Store in a silica glass or polyethylene bottle.

7.1.2 Apparatus

Ordinary laboratory apparatus and

7.1.2.1 One-mark volumetric flask, of capacity 1 000 ml, complying with ISO 1042.

7.1.2.2 One-mark pipette, of capacity 20 ml, complying with ISO 648.

7.1.2.3 Conical flask, wide neck, of capacity 250 ml.

7.1.2.4 Burette, of capacity 25 ml, graduated in 0,05 ml, complying with ISO 385-1, or an **automatic titrator.**

7.1.2.5 Beaker, of capacity 250 ml.

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[1] Thorin is the registered trade name for disodium-4-[(2-arsonophenyl)-azo]-3-hydroxynaphthalene-2,7-disulfonate.

7.1.3 Procedure

Concentrate the absorption solution (6.2) in the beaker (7.1.2.5), which shall contain at least 0,1 mg of sulfur, to about 20 ml by evaporation on a hotplate.

WARNING — Do not evaporate over a flame.

The concentration of the absorption solution on the hotplate should generally be done in a closed hood. Handle the beaker carefully because of the danger of explosion caused by peroxide formation. Wear safety glasses during this part of the handling.

Mix the concentrated absorption solution with four times its volume of 2-propanol (7.1.1.1). Add 6 to 8 drops of Thorin indicator solution (7.1.1.3), and up to 10 drops of the methylene blue solution (7.1.1.4) to this solution.

The ratio of Thorin indicator to methylene blue solution may be modified by the operator as and when required.

Titrate with the barium perchlorate standard volumetric solution (7.1.1.2) until the colour changes from yellow to a permanent pink, or in the presence of methylene blue, from green to purple/grey.

The Thorin end point is very difficult to see in some types of light, particularly fluorescent lighting and direct sunlight. Good results can be obtained by titrating in front of a daylight lamp.

The colour change can be readily detected photometrically at a wavelength of 520 nm.

7.1.4 Method of calculation

The total sulfur content in the natural gas is calculated as mass concentration $\varrho(\mathrm{S})$, in milligrams per cubic metre, using the equation

$$\varrho(\mathrm{S}) = \frac{V_1 c_1}{V_\mathrm{n}}$$

where

c_1 is the sulfur equivalent, in milligrams of S per millilitre, of the barium perchlorate solution (7.1.1.2);

V_1 is the volume, in millilitres, of the barium perchlorate solution (7.1.1.2) used in 7.1.3;

V_n is the volume, in cubic metres, of the gas sample under test (6.3).

Round the result to the nearest 0,5 mg/m^3.

7.2 Determination of sulfur content by turbidimetric titration

7.2.1 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

7.2.1.1 Barium chloride, standard volumetric solution.

Dissolve 0,38 g of barium chloride dihydrate ($BaCl_2,2H_2O$) in water in the 1 000 ml one-mark volumetric flask (7.2.2.3) and make up to the mark. Standardize the solution against 2,00 ml of sulfuric acid solution $[c(H_2SO_4) = 0{,}0025\ \mathrm{mol/l}]$ diluted with about 25 ml of water, by the method detailed in 7.2.3. Calculate the sulfur equivalent of the barium chloride solution in milligrams per millilitre.

1 ml of this standard volumetric solution is equivalent to approximately 0,050 mg of S.

7.2.1.2 Coagulant solution.

Dissolve 20 g of magnesium chloride hexahydrate ($MgCl_2,6H_2O$) and 3,5 g of ammonium chloride (NH_4Cl) in 1 000 ml of water. Adjust to a pH of 8,0 to 8,2 with concentrated ammonium hydroxide (NH_4OH) solution.

7.2.1.3 Methanol.

7.2.1.4 Sodium chloride, solution.

Dissolve 100 g of sodium chloride (NaCl) in 1 000 ml of water.

7.2.2 Apparatus

Ordinary laboratory apparatus and

7.2.2.1 Photometer, preferably a spectrophotometer having an effective band width of about 50 nm and equipped with a blue-sensitive photocell for use at 450 nm, or alternatively a **filter photometer** equipped with a colour filter having a maximum transmission at approximately 450 nm.

7.2.2.2 Absorption cells, with a thickness of 50 mm and a volume of at least 100 ml.

NOTE — The procedure described assumes an absorbance change of about 0,10 for each 100 µg of sulfur in 50 ml of solution measured in a 50 mm cell. Photometers employing cells of lesser thickness will not give the precision of measurement stated in this method.

7.2.2.3 One-mark volumetric flask, of capacity 1 000 ml, complying with ISO 1042.

7.2.2.4 One-mark pipettes, of capacities 1 ml, 2 ml, 5 ml, 20 ml and 25 ml, complying with ISO 648.

7.2.2.5 Burette, of capacity 25 ml, graduated in 0,05 ml, complying with ISO 385-1, or an **automatic titrator.**

7.2.2.6 Beaker, of capacity 250 ml.

7.2.3 Procedure

Add 1 ml of the sodium chloride solution (7.2.1.4) to the absorption solution (6.2) in the beaker (7.2.2.6). Evaporate on a hotplate until the contents reach a small volume which shall be not less than 1 ml.

WARNING — Do not evaporate over a flame (see 7.1.3.).

Allow the beaker and contents to cool, then add 5 ml of the coagulant solution (7.2.1.2) and ensure that the contents dissolve thoroughly. Add 20 ml of the methanol (7.2.1.3) and transfer the contents of the beaker quantitatively to a cell (7.2.2.2). Rinse the beaker with three 25 ml portions of methanol (7.2.1.3), add the rinsings to the cell and mix thoroughly with a paddle.

NOTE — Turbidity in the solution at this stage may be caused by the precipitation of magnesium phosphate, and should not interfere with the turbidimetric titration.

Insert the cell into the photometer (7.2.2.1) and record the initial galvanometer reading. Add the barium chloride solution (7.2.1.1) in small, equal increments, from the burette (7.2.2.5). In the case of sulfur contents below 0,05 mg/m^3, add 0,1 ml at a time; in the case of sulfur contents up to 0,15 mg/m^3 add 0,2 ml at a time; in the case of sulfur contents of more than 0,2 mg/m^3, add 0,5 ml at a time. After each addition, mix the liquid contents of the cell thoroughly with the paddle, then observe and record the galvanometer reading. Add at least five equal increments before the inflection point, and four increments subsequently.

To eliminate, as far as possible, the effect of outside light, it is recommended that the cell be covered after stirring following each addition of solution.

7.2.4 Method of calculation

Plot the volume, in millilitres, of the barium chloride solution (7.2.1.1) added against the corresponding galvanometer readings. Join the plotted points. The resulting curve consists of two sections; the intersection point of the tangents to the two branches is the equivalence point.

The total sulfur content in the natural gas is calculated as mass concentration $\varrho(\mathrm{S})$, in milligrams per cubic metre, using the equation

$$\varrho(\mathrm{S}) = \frac{V_2 c_2}{V_n}$$

where

c_2 is the sulfur equivalent, in milligrams of S per millilitre, of the barium chloride solution (7.2.1.1);

V_2 is the volume, in millilitres, of the barium chloride solution (7.2.1.1) at the equivalence point, used in 7.2.3;

V_n is the volume, in cubic metres, of the gas sample under test (see 6.3).

Round the result to the nearest 0,1 mg/m^3.

8 Precision

The precision of the method, as obtained by statistical examination of interlaboratory test results, is as follows.

8.1 Repeatability

The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test gas would, in the long run, in the normal and correct operation of the test method, exceed the values given in table 1 in only one case out of twenty.

8.2 Reproducibility

The difference between two single and independent results, obtained by different operators working in different laboratories on identical test gas would, in the long run, in the normal and correct operation of the test method, exceed the values given in table 1 in only one case out of twenty.

Table 1

Concentration range mg/m^3	Repeatability mg/m^3	Reproducibility mg/m^3
10 to 1 000	6	12

9 Test report

The test report shall include the following information :

a) a reference to this part of ISO 6326;

b) all information necessary for the complete identification of the sample (e.g. type and identification of the gas tested and the date of sampling);

c) the sampling method used;

d) the results and the method of calculation used;

e) details of any deviation from the procedure specified in this part of ISO 6326, or any circumstances that may have influenced the results.