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Sulphur for industrial use — Determination of total carbon content — Titrimetric method

Soufre à usage industriel — Dosage du carbone total — Méthode titrimétrique

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FOREWORD

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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.

International Standard ISO 2866 was drawn up by Technical Committee ISO/TC 47, *Chemistry,* and circulated to the Member Bodies in September 1972.

It has been approved by the Member Bodies of the following countries :

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This International Standard has also been approved by the International Union of Pure and Applied Chemistry (IUPAC).

No Member Body expressed disapproval of the document.

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INTERNATIONAL STANDARD ISO 2866-1974 (E)

Sulphur for industrial use — Determination of total carbon content — Titrimetric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a method for the determination of the total carbon content of sulphur for industrial use.

Two alternative methods are given for the final titration :

— a potentiometric method;

— a visual method.

2 PRINCIPLE

Combustion of the sulphur in a current of oxygen.

Oxidation and fixation of the sulphur dioxide and trioxide gases in chromic and sulphuric acid solutions.

Absorption of the carbon dioxide formed in a solution of barium hydroxide, followed by either potentiometric or visual titration in the presence of phenolphthalein and screened methyl orange as indicator.

3 REAGENTS

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

3.1 Pure oxygen (free from CO_2), in cylinders fitted with pressure-reducing valves.

3.2 Pure nitrogen (free from CO_2), in cylinders fitted with pressure-reducing valves.

3.3 Chromium(VI) oxide (CrO_3), 500 g/l solution.

3.4 Sulphuric acid, ρ approximately 1,84 g/ml, about 96 % (*m/m*) solution.

3.5 Soda-asbestos.

3.6 Platinized asbestos, containing 5 to 10 % of platinum.

3.7 Hydrogen peroxide, approximately 60 g/l solution (20 volumes).

3.8 Barium hydroxide, freshly prepared 0,05 N solution, containing a few drops of the phenolphthalein solution (3.12).

This solution shall be protected from atmospheric carbon dioxide by means of a trap containing soda-asbestos.

3.9 Hydrochloric acid, 0,05 N standard volumetric solution.

3.10 Sodium hydroxide, 0,05 N standard volumetric solution.

3.11 Screened methyl orange indicator.

Dissolve 0,25 g of methyl orange and 0,15 g of xylene cyanol FF in 50 ml of 95 % (*V/V*) ethanol.

3.12 Phenolphthalein, 10 g/l ethanolic solution.

Dissolve 1 g of phenolphthalein in 60 ml of 95 % (*V/V*) ethanol and dilute to 100 ml with water.

4 APPARATUS

Ordinary laboratory apparatus and

4.1 Combustion and absorption apparatus, giving complete and controlled combustion. An example of a suitable apparatus is shown in figure 1. This apparatus is fitted with spherical ground glass joints, lubricated with sulphuric acid, and comprises :

4.1.1 Mercury lute, fitted with an inner tube dipping 1 cm below the surface of the mercury (A).

4.1.2 Three U-tubes, with side arms and ground stoppers, of diameter 15 mm and height 150 mm (B_1, B_2, B_3).

4.1.3 Flow meter, suitable for oxygen flow measurements of between 20 and 200 ml/min (C).

4.1.4 Combustion tube, transparent silica, 60 cm long, external diameter 15 mm, reduced at one end over a length of 15 mm to an external diameter of 4 mm (D).

4.1.5 Furnace, capable of being maintained at 800 to 900 °C during the combustion (E).

4.1.6 Furnace, capable of being maintained at 400 to 450 °C during the combustion (F).

4.1.7 Six gas-washing bottles, Drechsel type (G_1 to G_6), 250 ml, two of which (G_5 and G_6) are tall and wide-necked (approximately 45 mm diameter).

4.1.8 Combustion boats, silica or fireclay, carbon-free.

For the potentiometric titration (see figure 2) :

4.2 Burette, 10 ml, graduated in 0,05 ml.

4.3 Potentiometer, with glass-calomel electrodes;

4.4 Electromagnetic stirrer.

5 PROCEDURE

5.1 Test portion

Weigh, to the nearest 0,01 g, into one of the boats (4.1.8), 1 to 1,5 g of the test sample, undried and completely passing a 250 μm sieve.

5.2 Preparation of the combustion apparatus

Fill the drying tubes B_1 and B_3 (4.1.2) with the soda-asbestos (3.5) between plugs of glass wool. Loosely fill tube B_2 (4.1.2) with glass wool.

NOTE — If the test portion, during the determination, releases so much acid vapour that the barium hydroxide is completely neutralized, repeat the operation using a sintered glass filter, with a porosity between 15 and 40 μm, instead of the U-tube B_2 filled with glass wool.

Leave the U-tube (4.1.2) valves closed until such time as it is necessary to open them.

Introduce at least 50 ml of the chromium(VI) oxide solution (3.3) into bottle G_2 (4.1.7) and at least 50 ml of the sulphuric acid (3.4) into bottles G_3 and G_4 (4.1.7).

Fill the combustion tube D (4.1.4) with the platinized asbestos (3.6) over a length slightly less than that of the furnace (4.1.6) hot zone.

Connect the various parts of the combustion apparatus as shown in figure 1.

5.3 Preparation of absorption apparatus

Displace all the air contained in the Drechsel bottles (4.1.7) with the oxygen (3.1). Introduce 20 ml of the barium hydroxide solution (3.8) into bottles G_5 and G_6 (4.1.7) and add sufficient water to obtain suitable bubbling of the gases. Carry out these operations as rapidly as possible, taking care to avoid any absorption of atmospheric carbon dioxide. Add 5 ml of the hydrogen peroxide solution (3.7) to each bottle in order to oxidize any sulphite which may have formed. Reconnect the Drechsel bottles to the absorption train.

5.4 Combustion

Light the furnace F (4.1.6) and pass the oxygen (3.1) into the apparatus at a flow rate of about 100 ml/min.

Approximately 30 min after the furnace (4.1.6) has reached the required temperature of 400 to 450 °C, connect the absorption apparatus (prepared according to the instructions in 5.3). Switch on the furnace E (4.1.5) and heat as described below for 30 min. Measure the carbon dioxide (blank test) as described in 5.5.1 (potentiometric titration) or 5.5.2 (visual titration). Repeat the operation until a negligible result is obtained, equivalent to less than 0,2 ml of the barium hydroxide solution (3.8).

While the furnace F (4.1.6) is being heated, weigh the test portion (5.1) into a boat (4.1.8). Fit the absorption apparatus (5.3) and introduce the boat into the cold part of the combustion tube D (4.1.4) which is opposite the furnace E (4.1.5).

By bringing the furnace E (4.1.5) slowly towards the boat, gradually heat the contents of the latter by burning the sulphur in such a way that traces of carbonaceous materials remain in the boat and inside the combustion tube D. If this combustion process is too rapid, the chromium(VI) oxide solution (3.3) in Drechsel bottle G_2 may be sucked back; should this tend to occur, increase the oxygen flow as necessary. If the sulphur sublimes outside the boat and condenses between the latter and the platinized asbestos, move the furnace E (4.1.5) so as to obtain complete combustion of the sulphur.

Once slow combustion of the sulphur has been carried out in this manner, replace the furnace E (4.1.5) in its original position (if necessary) and raise the temperature to 800 to 900 °C. Heat the tube and the boat it contains in order to burn the residual carbon and to decompose the carbonates present in the test portion.

Before switching off the furnaces E and F, pass a stream of oxygen through the tube for 30 min (to purge the apparatus).

NOTE — The combustion process described is intended to burn the sulphur into sulphur dioxide, which is oxidized by and absorbed in the chromic acid solution. At the same time, the carbonaceous materials and any carbonates are converted into carbon dioxide. The carbon dioxide emerges with the excess oxygen from bottle G_4, and is absorbed in bottles G_5 and G_6.

5.5 Determination of released carbon dioxide

When all the carbon dioxide has been absorbed (this being easily ascertained by observing the completion of precipitation in the Drechsel bottles), disconnect bottles G_5 and G_6.

Disconnect the head from each Drechsel bottle and rinse with a minimum of water, collecting the washing solutions together with the absorption solution.

Then measure separately the absorbed carbon dioxide in each of the two Drechsel bottles, according to one of the two following titration methods :

5.5.1 *Potentiometric titration*

Introduce a ferromagnetic bar, the pair of glass-calomel electrodes, the end of the burette (4.2) and a small nitrogen feed tube into the Drechsel bottle. Pass a current of the nitrogen (3.2) over the solution to be titrated, maintaining the current throughout the titration.

Place the electromagnetic stirrer (4.4) beneath the assembly and plot the potentiometric titration curve, titrating by means of the standard volumetric hydrochloric acid solution (3.9) until the pH value of the solution is in the region of 3.

In the vicinity of the two points of inflection of the curve (pH 9 to 6 and pH 4,5 to 3), add the standard volumetric hydrochloric acid solution (3.9), 0,05 ml by 0,05 ml, and plot the derived potentiometric curve $\frac{\Delta E}{\Delta V} = f(V)$, in order to deduce from it the two points of equivalence.

Carry out a blank titration under the same conditions using a similar volume of absorption solution.

5.5.2 *Visual titration*

Pass a current of the nitrogen (3.2) over the solution to be titrated, maintaining the current throughout the titration.

Neutralize the solution with the standard volumetric hydrochloric acid solution (3.9) in the presence of the phenolphthalein (3.12). Stir the solution vigorously and take the greatest care not to exceed the end point.

Then add to each bottle a few drops of the screened methyl orange indicator (3.11) and a measured excess (V_1 ml) of the standard volumetric hydrochloric acid solution (3.9). Shake well and back-titrate with the standard volumetric sodium hydroxide solution (3.10).

6 CALCULATION AND EXPRESSION OF RESULTS

6.1 Potentiometric titration

First calculate, for each Drechsel bottle G_5 and G_6, the volume V_0, in millilitres, of the standard volumetric hydrochloric acid solution (3.9) corresponding to the neutralization of CO_3 by the formula

$$V_0 = (V_2 - V_1) - (V_3 - V_4)$$

where

V_1 is the volume, in millilitres, of the standard volumetric hydrochloric acid solution (3.9) up to the first equivalence point of the actual test titration curve;

V_2 is the volume, in millilitres, of the standard volumetric hydrochloric acid solution (3.9) up to the second equivalence point of the actual test titration curve;

V_3 and V_4 are the volumes, in millilitres, of the standard volumetric hydrochloric acid solution (3.9) up to the two equivalence points of the blank test titration curve.

The total carbon content, expressed as a percentage by mass, is given by the formula

$$\frac{0,05 \times V_5 \times 6 \times 100}{1\,000 \times m} = \frac{0,03 \times V_5}{m}$$

where

V_5 is the sum of the volumes V_0, in millilitres, for the two Drechsel bottles G_5 and G_6;

m is the mass, in grams, of the test portion.

6.2 Visual titration

First calculate, for each Drechsel bottle G_5 and G_6, the volume V_0, in millilitres, of the standard volumetric hydrochloric acid solution (3.9) corresponding to the neutralization of CO_3, by the formula

$$V_0 = V_1 - V_2$$

where

V_1 is the volume, in millilitres, of the excess standard volumetric hydrochloric acid solution (3.9) added;

V_2 is the volume, in millilitres, of the standard volumetric sodium hydroxide solution (3.10) used for the back-titration.

The total carbon content, expressed as a percentage by mass, is given by the formula

$$\frac{0,03 \times V_3}{m}$$

where

V_3 is the sum of the volumes V_0, in millilitres, for the two Drechsel bottles G_5 and G_6;

m is the mass, in grams, of the test portion.

7 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard, or regarded as optional.

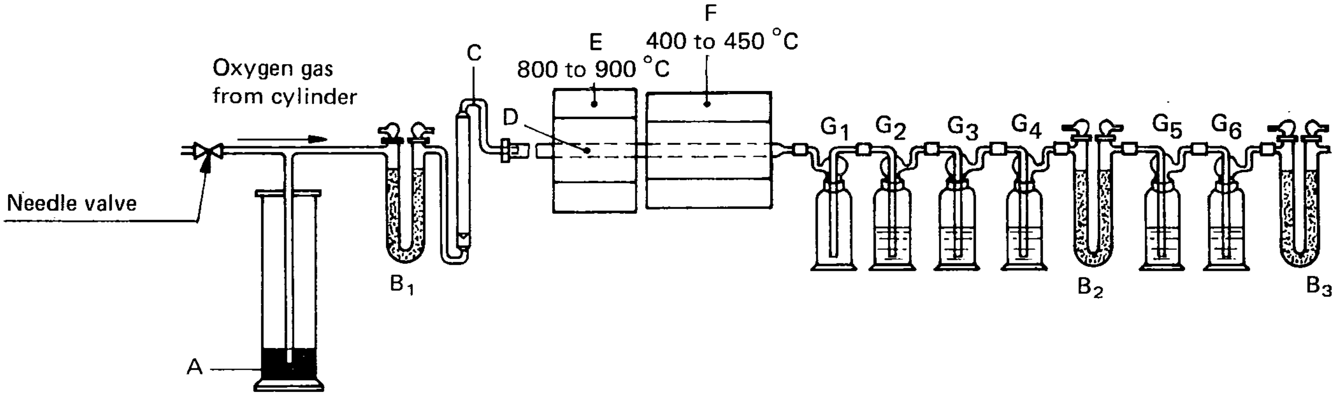

FIGURE 1 — **Example of combustion and absorption apparatus (4.1)**

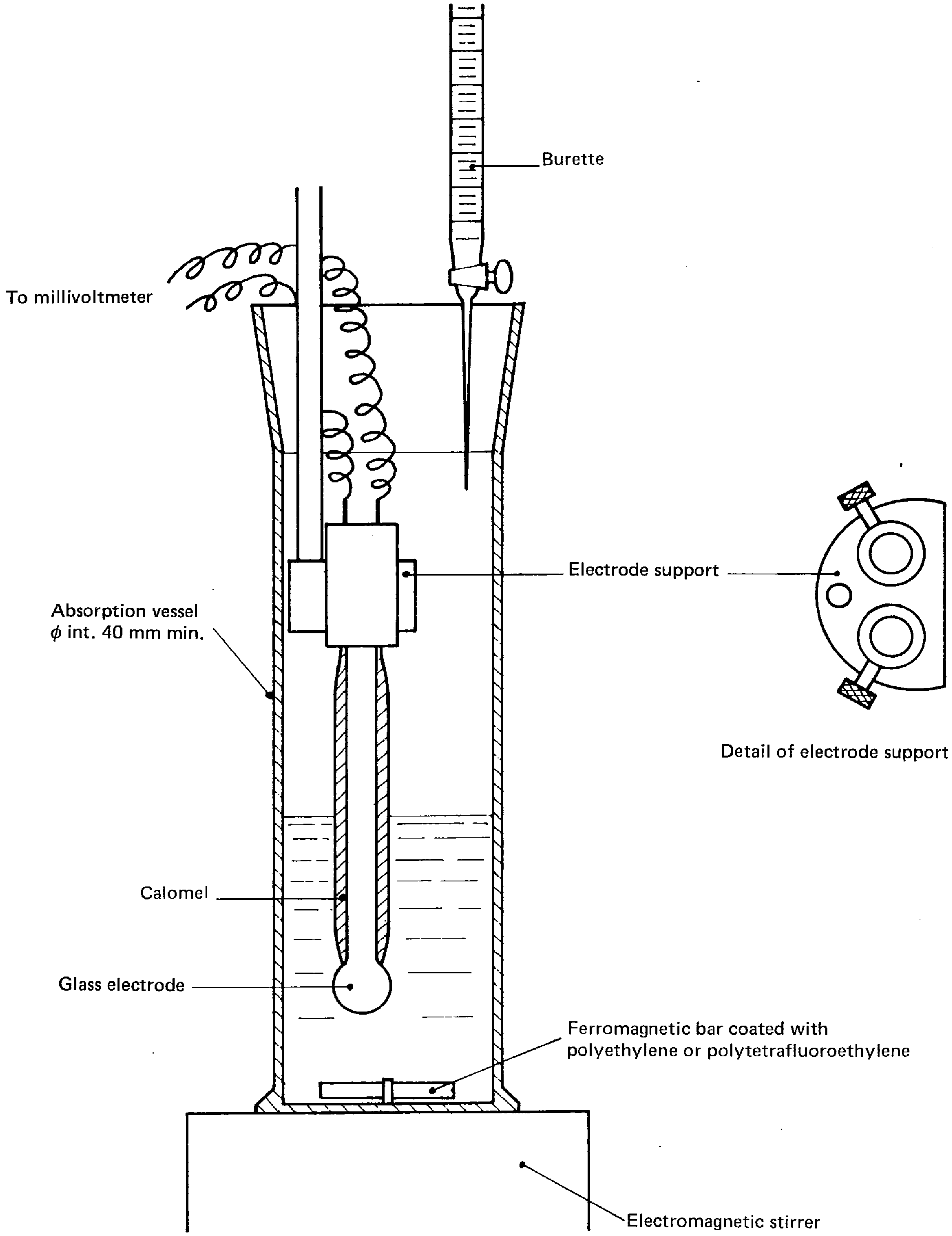

FIGURE 2 — **Diagram of apparatus for potentiometric titration**