

ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION R 157

DETERMINATION OF FORMS OF SULPHUR IN COAL

1st EDITION

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BRIEF HISTORY

The ISO Recommendation R 157, *Determination of Forms of Sulphur in Coal*, was drawn up by Technical Committee ISO/TC 27, *Solid Mineral Fuels*, the Secretariat of which is held by the British Standards Institution (B.S.I.).

At the second meeting of the Technical Committee, held in London, in December 1951, the question of the determination of forms of sulphur in coal was discussed for the first time, and in July 1952, a draft proposal was circulated.

At the third meeting of ISO/TC 27, held in London, in November 1953, a second draft proposal, modified in line with the comments received, was submitted to the Technical Committee, together with a possible alternative method based on comments from Germany, but there was not enough time to discuss them adequately. The members of the Committee were asked to send in their comments in writing, and the subject was also taken up by Working Groupe No. 3, *Sulphur*. At the latter's first meeting, in May 1954, it was agreed, after practical demonstrations, that the reduction method could be regarded as a satisfactory alternative to the oxydation method for the determination of pyritic sulphur.

A third draft proposal was worked out and discussed at the second meeting of Working Group No. 3, in October 1954, before being circulated to the members of ISO/TC 27 in January 1955. This draft, which contained alternative methods for sulfate sulphur (gravimetric and titrimetric) and alternative methods for pyritic sulphur (oxidation and reduction), was examined, together with a report on the experimental work on which was based, at the fourth meeting of ISO/TC 27, held in Stockholm in June 1955. It was decided—with a reservation by France, which would have preferred to see only one method standardized, to use the third draft proposal as the basis for setting up a Draft ISO Recommendation for the determination of forms of sulphur.

This draft proposal was circulated in March 1956 to all the members of ISO/TC 27 for ratification and, with minor changes, was adopted as a Draft ISO Recommendation.

On 29 June 1957, the Draft ISO Recommendation (N° 169) was distributed to all the ISO Member Bodies and was approved, subject to some modifications, by the following 24 (out of a total of 38) Member Bodies:

Austria	India	* Portugal
Belgium	* Ireland	Romania
* Canada	* Italy	Spain
Czechoslovakia	Japan	Sweden
Denmark	Mexico	* Switzerland
* Germany	Netherlands	United Kingdom
* Greece	* New Zealand	* U.S.A.
Hungary	* Poland	* Yugoslavia

One Member Body opposed the approval of the Draft: France.

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in June 1960, to accept it as an ISO RECOMMENDATION.

* These Member Bodies stated that they had no objection to the Draft being approved.

DETERMINATION OF FORMS OF SULPHUR IN COAL

1. PRINCIPLE

The principle to be applied for the determination of sulphur in coal depends on the form in which the sulphur is combined in the coal.

Sulphur is usually combined in coal in three ways, as

inorganic sulphates,
iron pyrites (FeS_2) and
organic sulphur compounds.

The amounts of sulphur so combined are known respectively as

sulphate sulphur,
pyritic sulphur,
organic sulphur.

- 1.1 Sulphate sulphur** is determined by extracting coal with dilute hydrochloric acid and determining the sulphur in the extract,

either gravimetrically, see section 2, Gravimetric Method,
or titrimetrically, see section 3, Titrimetric Method.

- 1.2 Pyritic sulphur** is insoluble in dilute hydrochloric acid, but it is quantitatively dissolved by dilute nitric acid under the experimental conditions described.

It is conveniently determined by an indirect method, that is by determining the amount of iron combined in the pyritic state and calculating the amount of sulphur associated with this iron, see section 4, Oxidation Method.

Alternatively, the coal is finely crushed to release the particles of pyrites, the sulphur in which is reduced to hydrogen sulphide by reaction with nascent hydrogen and is absorbed in cadmium acetate and determined iodometrically, see section 5, Reduction Method.

- 1.3 Organic sulphur** is calculated by deducting the sum of percentages of "sulphate" and "pyritic" sulphur from the total sulphur in the coal, see section 6.

2. SULPHATE SULPHUR — GRAVIMETRIC METHOD

2.1 Apparatus

All graduated apparatus should be of the best analytical quality obtainable, and the balance used should be sensitive to 0.1 mg.

2.1.1 *Electrically heated muffle furnace*, capable of maintaining a substantially uniform temperature zone at $800 \pm 25^\circ\text{C}$, and a flat plate, 6 mm thick, of silica (or other suitable insulating material), which fits easily in the muffle, or

2.1.2 *Air oven*, capable of being maintained at $130 \pm 10^\circ\text{C}$, for drying Gooch filters.

2.1.3 *Cold finger condenser* (see Fig. 1 below).

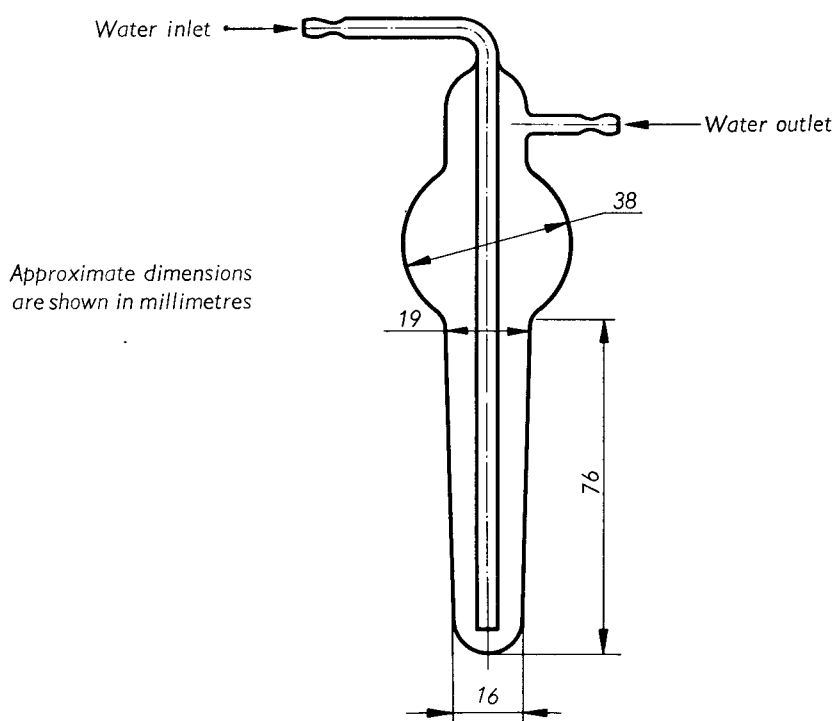


FIG. 1. — Cold finger condenser
for the determination of sulphate and pyritic sulphur

2.2 Reagents

All reagents are to be of analytical reagent quality and distilled water is to be used throughout.

2.2.1 *Hydrochloric acid*, specific gravity d 1.18.

2.2.2 *Hydrochloric acid*. Dilute 420 ml of the hydrochloric acid (2.2.1) to 1 litre with water.

2.2.3 *Hydrochloric acid*. Dilute 42 ml of the hydrochloric acid (2.2.1) to 1 litre with water.

2.2.4 *Barium chloride solution*, 8.5 per cent (weight/volume). Dissolve 100 g of barium chloride dihydrate in water and dilute to 1 litre. Filter before use through a close-textured, double acid-washed filter paper or filter paper pad.

2.2.5 *Ammonia solution*, specific gravity d 0.88 or nearest obtainable.

2.2.6 *Bromine water*. Prepare a saturated solution of bromine in water.

2.2.7 Standard sulphate solution. Dissolve 0.600 0 g of potassium sulphate in water and dilute to 1 000 ml. 10 ml of standard sulphate solution $\approx$ 0.008 0 g of BaSO_4 .

2.2.8 Methyl orange indicator solution. Dissolve 0.5 g of dimethyl-amino-azobenzene-sulphonic acid (methyl orange) in 1 litre of water; filter the cold solution if a precipitate separates.

2.3 Procedure

Before commencing the determination, mix the air-dried sample of coal, ground to pass a sieve of 0.2 mm aperture, thoroughly for at least one minute, preferably by mechanical means.

Weigh accurately about 5 g of the sample, transfer to a 250 ml conical flask, add 50 ml of the hydrochloric acid (2.2.2) and fit a cold finger condenser (see Fig. 1) into the neck of the flask. Boil for 30 minutes and filter through a medium-textured, double acid-washed paper. Wash 6 times with the hydrochloric acid (2.2.3), using a total quantity of about 20 ml. Discard the residual coal.

Add 1 ml of the bromine water (2.2.6) to the filtrate and boil for 5 minutes to ensure that all the iron is in the ferric state. Precipitate the iron by adding the ammonia solution (2.2.5) in a slow stream until a slight excess is present and add 5 ml in excess. Filter on a fast toughened filter paper into a 250 ml beaker. Wash with hot water, preserving the precipitate (precipitate A) for the determination of non-pyritic iron, if the Oxidation Method is to be employed for the determination of pyritic sulphur (see clause 4.3, last paragraph).

To the filtrate add 2 or 3 drops of the methyl orange indicator solution (2.2.8) and then, cautiously, add the hydrochloric acid (2.2.1) until the colour of the solution changes, then add 1 ml of acid in excess. The volume of the solution should be between 150 and 250 ml.

Add 10.0 ml of the standard sulphate solution (2.2.7), heat the covered beaker until the solution boils and then reduce the heating slightly until ebullition ceases. Add 10 ml of the cold barium chloride solution (2.2.4) from a pipette with a delivery time of approximately 20 seconds, so that the barium chloride falls into the centre of the hot solution, which is being agitated. Keep the solution just below boiling point, without agitation, for 30 minutes (see Note 1, page 6).

Filter, using one of the following techniques (see Note 2, page 6):

1. By gravity through an ashless, close-textured, double acid-washed filter paper of 10 to 12.5 cm diameter in a fluted, long-stemmed 60° funnel, or
2. By gravity through a filter paper pad prepared from ashless, double acid-washed paper, or
3. Under suction, using asbestos in a Gooch crucible, previously dried for 1 hour at $130 \pm 10^\circ\text{C}$ and weighed.

Wash the filter with hot water, using not more than 250 ml, until the last 20 ml of the washings give not more than a faint opalescence with silver nitrate solution.

Place the wet filter paper (from technique 1 or 2) in a previously ignited and weighed silica, porcelain or platinum capsule on the silica plate and insert into the muffle furnace for 15 minutes at $800 \pm 25^\circ\text{C}$ (see Note 3, page 6), then allow to cool and weigh. If a Gooch crucible is used (technique 3), dry for 1 hour at $130 \pm 10^\circ\text{C}$, then allow to cool and weigh.

NOTES

1. **Period of standing.** It has been shown that complete recovery of the barium sulphate can be made by filtering after 30 minutes under the conditions recommended, namely, in the presence of hydrochloric acid of concentration approximately 0.05 N and a large excess of barium ions. Under these conditions, the precipitate of barium sulphate should settle during the 30 minutes standing time mentioned above.

2. **Filtration of the precipitate.** Rapid filtration is obtained by any of the techniques 1, 2 or 3, indicated in clause 2.3.

Technique 1. A filter circle should be carefully folded to fit the funnel.

Technique 2. To prepare the filter paper pad, shake double acid-washed filter paper clippings, in pieces of approximately 1 cm² area, with distilled water in a bottle until the paper is thoroughly disintegrated.

Place a 2.5 cm porcelain filter cone in a 7.5 cm funnel, close the stem of the funnel with a finger and add distilled water until the cone is immersed and the funnel stem is full. Shake onto the cone sufficient pulp to form a pad 5 mm thick and level it with a flat-ended glass rod. Allow the excess water to drain away by removing the finger from the stem of the funnel and lightly tamp the pad round the edges with the glass rod as drainage ceases. A final wash with water renders the filter ready for use.

After transferring the filter paper pad to the silica capsule, wipe the funnel successively with two halves of a circle of ashless filter paper, which are then incinerated with the pad.

Technique 3. The Gooch crucible should be used with specially prepared filtration asbestos.

3. **Ignition.** Under these conditions ignition of the wet filter paper is achieved rapidly; with mechanical loss is avoided by the use of a thick insulating plate.

- 2.3.1 **Blank determination.** Carry out a blank determination under the same conditions, but omitting the coal. Add 10.0 ml of the standard sulphate solution (2.2.7) to the filtrate before adding the methyl orange indicator solution (2.2.8). The weight of the barium sulphate found in the blank determination is deducted from that obtained in the full determination.

2.4 Calculation of results

If W = weight of sample, expressed in grammes,

a = weight of barium sulphate found in the full determination, expressed in grammes,

b = weight of barium sulphate found in the blank determination, expressed in grammes,

S_s = percentage of sulphate sulphur in the sample,

$$\text{then} \quad S_s = \frac{13.74 (a - b)}{W}$$

2.5 Tolerances

The results of duplicate determinations carried out at different times in the same laboratory, on the same sample, by the same operator using the same apparatus, should not differ by more than 0.02 per cent of sulphate sulphur.

The means of the results of duplicate determinations carried out in different laboratories on representative samples taken from the same bulk after the last stage of reduction should not differ by more than 0.03 per cent of sulphate sulphur.