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ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION
R 159

DETERMINATION OF TOTAL SULPHUR IN COAL BY THE STRAMBI METHOD

1st EDITION
June 1960

For each individual country the only valid standard is the national standard of that country.

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BRIEF HISTORY

The ISO Recommendation R 159, *Determination of Total Sulphur in Coal by the Strambi Method*, 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 its first meeting, held in London, in March 1950, Technical Committee ISO/TC 27 considered the Strambi (bomb calorimeter) method for the determination of total sulphur. The general applicability of the method not then being established, the Committee, after deciding upon various technical points, deferred further consideration of it.

By the time of the second meeting, held in London, in December 1951, evidence had accumulated in support of the Strambi method, and it was agreed that Italy and the United Kingdom should exchange samples and conduct further comparative tests on the Eschka and the Strambi methods.

The first draft proposal was considered at the third meeting of the Technical Committee, held in London, in November 1953. No general agreement could be reached, especially with regard to the extraction procedure and the behavior of coals containing barium. The Committee called for further investigation of the method, and set up Working Group No. 3, *Sulphur*, to conduct the necessary practical tests. The Committee also decided that a Draft ISO Recommendation should be developped, subject to the Working Group's agreement on technical points.

The Working Group met in May and in October 1954, and reached agreement on all the major points at issue. A revised draft was circulated to the Working Group in June 1955, and as a result of that consultation further changes were made.

A draft proposal for an ISO Recommendation was circulated to the members of Technical Committee ISO/TC 27, in September 1956 and was unanimously approved as a Draft ISO Recommendation.

On 17 July 1957, the Draft ISO Recommendation (No. 176) was distributed to all the ISO Member Bodies and was approved, by the following 26 (out of a total of 39) Member Bodies:

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

Two Member Bodies opposed the approval of the Draft: France, U.S.S.R.

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.

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

ISO Recommendation R 159 June 1960

DETERMINATION OF TOTAL SULPHUR IN COAL BY THE STRAMBI METHOD

1. PRINCIPLE

The sample, intimately mixed with Eschka mixture, is burned in a calorimeter bomb made of austenitic steel, filled with oxygen at a pressure of 25 atmospheres and containing ammonium carbonate solution. Complete conversion to sulphate of the sulphur in the combustion products is ensured by the addition of hydrogen peroxide, and the sulphate is extracted with hot water. The sulphate is determined either

gravimetrically as barium sulphate or
titrimetrically using barium chromate.

2. RANGE

2.1 Gravimetric method. Up to 20 per cent of sulphur.

2.2 Titrimetric method. From 1.2 to 5 per cent of sulphur.

3. APPARATUS

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

3.1 For both methods

3.1.1 *Calorimeter bomb*, as used in the determination of the calorific value of coal. Sealing washers of lead are not to be used.

3.1.2 *Platinum crucible.* The internal diameter of the base of the crucible should be not less than 20 mm; the diameter of the top of the crucible should be not less than that of the base.

3.1.3 *Ignition wire*, of platinum or nickel chromium alloy.

3.1.4 *Cotton thread.*

3.1.5 *Glass rods*, with flattened ends about 10 mm in diameter.

3.2 For gravimetric method

3.2.1 *Electrically heated muffle furnace*, with a substantially uniform hot zone at 800 ± 25 °C, and a flat plate, of silica (or other suitable insulating material), 6 mm thick, which fits easily in the muffle, or

3.2.2 *Air-oven*, capable of being maintained at 130 ± 10 °C, for drying Gooch filters.

4. REAGENTS

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

4.1 For both methods

4.1.1 *Eschka mixture.* Mix two parts by weight of light, calcined magnesium oxide with one part of anhydrous sodium or potassium carbonate. The mixture should entirely pass a test sieve of 0.2 mm nominal aperture and its bulk density should be not greater than 0.50 g/ml. The bulk density may be conveniently determined as follows:

Place 50 g of the mixture in a 250 ml graduated cylinder; hold the cylinder in a vertical position and tap it gently 100 times on a bench or table top; measure the volume occupied by the mixture.

4.1.2 *Ammonium carbonate solution*, 10 per cent (weight/volume). Dissolve 10 g of ammonium carbonate in 100 ml of water.

4.1.3 *Hydrogen peroxide*, 30 per cent (weight/volume) ("100 vol.").

4.1.4 *Sodium hydroxide solution*, 8 per cent (weight/volume). Dissolve 80 g of sodium hydroxide in 1 litre of water.

4.1.5 *Hydrochloric acid*, specific gravity *d* 1.18.

4.1.6 *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 ≡ 0.008 0 g $BaSO_4$
≡ 1.033 ml of 0.1 N sodium thiosulphate solution.

4.2 For gravimetric method

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

4.2.2 *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 fine-textured, double acid-washed filter paper or filter paper pad.

4.2.3 *Methyl red indicator solution.* Dissolve 1 g of o-carboxybenzene-azo-dimethyl aniline (methyl red) in 600 ml of ethanol or industrial methylated spirit and dilute to 1 litre with water.

4.3 For titrimetric method

4.3.1 *Potassium iodide.*

4.3.2 *Barium chromate solution*, 3 per cent (weight/volume). To 30 g of barium chromate add 100 ml of water and 100 ml of perchloric acid (specific gravity *d* 1.54) and warm until solution is complete. Dilute the solution to 1 litre and filter into a storage bottle through a fine-textured double acid-washed filter paper or filter paper pad. Store overnight before using.

The solution prepared from commercially available barium chromate should be tested for suitability. This is done by using it to carry out duplicate determinations, by the method described under "Procedure" (see section 5) on accurately weighed portions of between 0.13 and 0.14 g of potassium sulphate. If the mean of the results, expressed as per cent of the amount of sulphur taken, is less than 99.5 or greater than 100.5, the barium chromate in question should be rejected.

A satisfactory solution may be prepared by the following method: Dissolve 28.92 g of barium chloride dihydrate in 500 ml of water. Dissolve 23.00 g of potassium chromate in 500 ml of water. Heat both solutions almost to boiling point and add the barium chloride solution slowly to the potassium chromate solution, stirring during the addition. Boil for 5 minutes, filter by suction through a fine-textured double acid-washed filter paper supported in a Buchner funnel and wash with hot water until the last 20 ml of the washings give no more than a faint trace of opalescence with silver nitrate solution.

Wash the precipitate by means of a jet of water into a 2 litre beaker, add 200 ml of water and 100 ml of perchloric acid (specific gravity *d* 1.54) and warm until solution is complete. Dilute the solution to 1 litre with water and filter into a storage bottle through a fine-textured double acid-washed filter paper or filter paper pad.

4.3.3 *Sodium acetate solution*, 13.6 per cent (weight/volume). Dissolve either 136 g of anhydrous sodium acetate or 225 g of the trihydrate in water and dilute to 1 litre.

4.3.4 *Ammonia solution.* Dilute ammonia solution (specific gravity *d* 0.88 or nearest obtainable) with an equal volume of water. Store this solution over calcium oxide to remove carbonate.

4.3.5 *Sodium acetate solution*, 0.9 per cent (weight/volume). Dissolve 9 g of anhydrous sodium acetate or 15 g of the trihydrate in water and dilute to 1 litre.

4.3.6 *Sodium thiosulphate solution*, approximately 0.1 N. Dissolve 25 g of sodium thiosulphate pentahydrate in freshly boiled water, add 1 ml of chloroform and dilute to 1 000 ml with water. Standardize this solution before use with 0.1 N iodine or with 0.1 N potassium iodate solution in the presence of a trace of potassium iodide.

4.3.7 *Mixed indicator solution*

SOLUTION A. Dissolve 0.125 g of o-carboxybenzene-azo-dimethyl aniline (methyl red) in 60 ml of ethanol or industrial methylated spirit and dilute to 100 ml with water.

SOLUTION B. Dissolve 0.083 g of 3:7 bis-dimethylamino-phenazothionium chloride (methylene blue) in 100 ml of ethanol or industrial methylated spirit. Store in a dark glass bottle.

Mix equal volumes of solution A and B. Discard the mixed solution after one week.

4.3.8 *Phenol red indicator solution.* Grind 1 g of phenolsulphonephthalein (phenol red) with 28.4 ml of a 0.4 per cent sodium hydroxide solution and dilute to 1 litre with water.

4.3.9 *Starch indicator solution*, 1 per cent (weight/volume). Suspend 1 g of soluble starch in 5 ml of water, then add the suspension rapidly to 90 ml of boiling water. Boil for 1 minute and cool. Prepare fresh daily.

5. PROCEDURE

5.1 Preparation of solution

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.

Cover the bottom of the platinum bomb crucible uniformly with 0.2 g of the Eschka mixture (4.1.1). Weigh accurately about 0.5 g of the sample and mix it intimately with 1.0 g of the Eschka mixture (4.1.1) in a suitable vessel. Transfer the mixture to the bomb crucible, leaving the mass as light and open as possible.

Fit the bomb with ignition wire and fuse of cotton thread, place in it 5 ml of the ammonium carbonate solution (4.1.2) and insert the charged crucible. Fill the bomb with oxygen to a pressure of 25 atmospheres, completely immerse it in cold water and ignite the charge.

Allow the bomb and contents to stand for at least 15 minutes after the ignition, remove from the water, then vent the gases at a uniform rate, taking at least one minute for this operation. Transfer the contents of the crucible and bomb to a 400 ml beaker containing 10 to 20 ml of water, 2 or 3 drops of the hydrogen peroxide (4.1.3) and 5 ml of the sodium hydroxide solution (4.1.4). Wash the crucible and the interior of the bomb, including the valve, with hot water, adding these washings to the contents of the beaker. Finely crush the insoluble material with a flat-ended glass rod.

Place a cover glass on the beaker and boil for approximately 30 minutes. Allow the solid material to settle and decant the liquid through a filter, collecting the filtrate in a 400 ml beaker (see note below). Wash the residue in the beaker at least four times with hot water, followed each time by decantation through the filter, then transfer the residue to the filter and wash a further three times with hot water.

The determination may be completed by either of the procedures described under clauses 5.2 and 5.3.

NOTE. A medium-textured double acid-washed filter paper or a filter paper pad is recommended for speed of filtration.

To prepare the filter paper pad, shake double acid-washed filter paper clippings, in pieces of approximately 1 cm^2 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.

5.2 Gravimetric method

Add to the solution 2 or 3 drops of the methyl red indicator solution (4.2.3), cautiously add sufficient of the hydrochloric acid (4.1.5) until the colour of the solution changes, then add 1 ml of acid in excess. The volume of the solution should be between 150 ml and 250 ml.

Heat the covered beaker until the solution boils, boil for 5 minutes to remove carbon dioxide, then reduce the heating slightly until ebullition ceases. Add 10 ml of the cold barium chloride solution (4.2.2) 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 for 30 minutes, without agitation (see Note 1 hereafter).