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DETERMINATION OF TOTAL SULPHUR IN COAL BY THE ESCHKA METHOD

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BRIEF HISTORY

The ISO Recommandation R 334, *Determination of Total Sulphur in Coal by the Eschka 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.).

Work on this question by the Technical Committee began in 1950 and led, in 1957, to the adoption of a Draft ISO Recommendation.

In May 1958, this Draft ISO Recommendation (No. 237) was circulated to all the ISO Member Bodies for enquiry. It was approved by the following Member Bodies:

Austria
Belgium
Burma
Chile
Czechoslovakia
Denmark
Germany
Greece
India
Italy
Japan
Mexico
Netherlands
New Zealand
Portugal
Romania
Spain
Turkey
United Kingdom
U.S.S.R.
Yugoslavia

Two Member Bodies opposed the approval of the Draft:

Canada, France.

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in August 1963, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 334 August 1963

DETERMINATION OF TOTAL SULPHUR IN COAL BY THE ESCHKA METHOD

1. PRINCIPLE

The sample of coal is ignited in intimate contact with Eschka mixture in an oxidizing atmosphere, to remove combustible matter and to convert the sulphur to sulphate. This is then extracted and determined by one of the two following methods:

(1) *Gravimetric method*, by precipitation with barium chloride;

(2) *Titrimetric method*, by precipitation with barium chromate, followed by iodometric determination of the chromate passing into solution.

2. SIZE OF SAMPLE

The mass of the sample required varies according to the sulphur content of the coal and the method chosen for determining the sulphate.

Sample mass	Range of total sulphur content	
	Gravimetric method	Titrimetric method
grammes	per cent	per cent
1	0.1 to 5	0.6 to 2.5
0.5	5 to 10	1.2 to 5
0.25	10 to 20	2.4 to 10
0.1	—	5 to 25

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 *Electrically* * *heated muffle furnace*, with a zone of substantially uniform temperature at 800 ± 25 °C and a ventilation rate of about 5 air changes per minute (see Note 1, page 12).

3.1.2 *Crucibles* of platinum or glazed porcelain, of approximately 25 ml capacity.

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* Although an electrically heated muffle furnace is recommended, a gas-heated furnace may be used, if precautions are taken to prevent contamination by sulphur that may be present in the combustion gases.

3.2 For gravimetric method

3.2.1 *Insulating plate*, 6 mm thick, of silica or other suitable material, which fits easily in the muffle.

3.2.2 *Crucibles* of fused silica or platinum, or Gooch crucibles of glazed porcelain.

4. REAGENTS

All reagents should be of analytical reagent quality, and distilled water should be used throughout.

4.1 For both methods

4.1.1 *Eschka mixture.* Mix two parts by mass of light, calcined magnesium oxide with one part by mass of anhydrous sodium (or potassium) carbonate. The mixture should entirely pass a test sieve of 0.2 mm aperture.

4.1.2 *Hydrochloric acid*, relative density d 1.18.

4.1.3 *Standard sulphate solution.* Dissolve 0.6000 g of potassium sulphate in water and dilute to 1000 ml.

10 ml of this solution corresponds to:

0.0080 g of barium sulphate or
1.033 ml of 0.1 N sodium thiosulphate solution.

4.2 For gravimetric method

4.2.1 *Barium chloride solution*, 8.5 per cent (mass/volume). Dissolve 100 g of barium chloride dihydrate in water and dilute to 1 litre. Filter the solution through a fine-textured double acid-washed paper.

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

4.3 For gravimetric acid-extraction method

4.3.1 *Ammonia solution*, relative density d 0.88, or the nearest obtainable.

4.4 For gravimetric aqueous-extraction method and titrimetric method

4.4.1 *Hydrogen peroxide*, 30 per cent (mass/volume) ("100 volumes").

4.5 For titrimetric method

4.5.1 *Potassium iodide.*

4.5.2 *Sodium hydroxide solution*, 8 per cent (mass/volume). Dissolve 80 g of sodium hydroxide in water and dilute to 1 litre.

4.5.3 *Barium chromate solution*, 3 per cent (mass/volume). To 30 g of barium chromate add 100 ml of water and 100 ml of perchloric acid (relative density *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 a 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 section 5, "Procedure", on accurately weighed portions of between 0.13 g and 0.14 g of potassium sulphate. If the mean of the results, expressed as a percentage of the amount of sulphur taken, is less than 99.5 or greater than 100.5, the barium chromate 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 distilled 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 distilled water and 100 ml of perchloric acid (relative density *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 a filter paper pad.

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

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

4.5.6 *Diluted ammonia solution.* Dilute the ammonia solution (4.3.1) (relative density *d* 0.88) with an equal volume of water; dilute other strengths appropriately. Store this solution over calcium oxide to remove carbonate.

4.5.7 *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 1000 ml with water. Standardize this solution before use against 0.1 N potassium iodate in the presence of a trace of potassium iodide.

4.5.8 *Mixed indicator solution*

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

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

Mix equal volumes of solution A and solution B. Do not use the mixed solution after more than one week.

4.5.9 *Phenol red indicator solution.* Grind 1 g of phenol-sulphonphthalein (phenol red) with 28.4 ml of 0.4 per cent sodium hydroxide solution and dilute to 1 litre.

4.5.10 *Starch indicator solution*, 1 per cent (mass/volume). Suspend 1 g of soluble starch in 5 ml of water and 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, for at least 1 minute, preferably by mechanical means.

Cover the bottom of the 25 ml crucible uniformly with 0.5 g of the Eschka mixture (4.1.1). Weigh accurately 1 g, 0.5 g, 0.25 g or 0.1 g of the sample (according to the expected sulphur content and the method of determination) and mix it intimately with 2.5 g of the Eschka mixture (4.1.1) in a suitable vessel. Transfer the mixture to the 25 ml crucible; level the contents by tapping the crucible gently on the bench and cover the contents uniformly with 1.0 g of the Eschka mixture (4.1.1) (see Note 2, page 12).

Place the charged crucible (and any others up to the limit of the muffle capacity) in the cold furnace and raise the temperature to 800 ± 25 °C in about 1 hour, maintaining this temperature for a further 1½ hours. Withdraw the crucible (or crucibles) and allow to cool (see Note 3, page 12).

Transfer the ignited mixture from the crucible to a 400 ml beaker containing 25 to 30 ml of water. If unburnt particles are present, the determination should be rejected. Wash out the crucible thoroughly with hot water, using about 50 ml, and add the washings to the contents of the beaker.

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

5.2 Gravimetric method

Extract the sulphate in the residue by either of the two methods below:

Acid extraction, see clause 5.2.1
Aqueous extraction, see clause 5.2.2.

5.2.1 *Acid extraction.* Place a cover glass on the beaker and then carefully add sufficient of the hydrochloric acid (4.1.2) — 17 ml will normally be required—to dissolve the solid matter, warming the contents of the beaker to effect solution. Boil for 5 minutes to expel carbon dioxide and filter, collecting the filtrate in a 400 ml conical beaker (see Note 4, page 12). Wash the filter with five 20 ml portions of hot water.

To the combined filtrate and washings add 2 or 3 drops of the methyl red indicator (4.2.2) and then, cautiously, add the ammonia solution (4.3.1) until the colour of the indicator changes and a trace of precipitate is formed. Add sufficient of the hydrochloric acid (4.1.2) to just redissolve the precipitate and then add 1 ml in excess.

5.2.2 *Aqueous extraction.* Add to the contents of the beaker 1 ml of the hydrogen peroxide (4.4.1). Heat at 80 °C for 30 minutes and filter, collecting the filtrate in a 400 ml conical beaker (see Note 4, page 12). Wash the filter with five 20 ml portions of hot water.

Boil to remove hydrogen peroxide, using methyl red (4.2.2) to indicate completeness of removal. Add the hydrochloric acid (4.1.2) dropwise until the colour changes to red and then add 1 ml in excess. Boil for 5 minutes to expel carbon dioxide.

After either of these extractions, the volume of the solution should be between 150 and 250 ml. Heat the covered beaker until the solution boils and then reduce the heating slightly until ebullition of the solution ceases. Then add 10 ml of the cold barium chloride solution (4.2.1) 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 (see Note 5, page 12).

Filter, using one of the following techniques (see Note 6, page 12):

(1) By gravity, through an ashless, fine-textured, double acid-washed paper in a fluted, long-stemmed 60° funnel;

(2) By gravity, through a filter paper pad prepared from ashless, double acid-washed paper (see Note 4, page 12);

(3) By suction, using asbestos in a Gooch crucible which has been previously dried for 1 hour at a temperature of 130 ± 10 °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 or platinum crucible on the insulating plate and insert into the muffle furnace for 15 minutes at 800 ± 25 °C (see Note 7, page 12). If a Gooch crucible is used (technique (3)), dry previously for 1 hour at 130 ± 10 °C, then allow to cool and weigh.

5.2.3 *Blank determination.* Carry out a blank determination under the same conditions, but omitting the coal. Add 10 ml of the standard sulphate solution (4.1.3) to the filtrate before adding the methyl red indicator solution (4.2.2). The mass of the barium sulphate obtained in the blank determination, less the equivalent of the standard sulphate solution added, is deducted from that obtained in the full determination.

5.3 Titrimetric method

Add to the contents of the beaker 1 ml of the hydrogen peroxide (4.4.1). Heat at 80 °C for 30 minutes and filter, collecting the filtrate in a 400 ml conical beaker (see Note 4, page 12). Wash the filter five times with 20 ml portions of hot water each time.

Boil the combined filtrate and washings for 10 minutes. Add 2 or 3 drops of the mixed indicator solution (4.5.8) or the phenol red indicator solution (4.5.9) and acidify by the careful addition of 5 ml of the hydrochloric acid (4.1.2). Boil the solution until the volume is reduced to between 80 and 100 ml. Whilst still hot, add the sodium hydroxide solution (4.5.2) dropwise, until the solution is just alkaline.

Add 10 ml of the barium chromate solution (4.5.3) dropwise, from a pipette, to the hot solution, stirring during the addition, and boil for 2 or 3 minutes. Add 10 ml of the sodium acetate solution (4.5.4). Boil for 2 or 3 minutes, then carefully add the ammonia solution (4.5.6) until the solution is distinctly alkaline; continue boiling until the excess ammonia is expelled, remove from the hot plate and allow to cool for 20 minutes.

Filter the cool solution into a 400 ml conical beaker or flask (see Note 6, page 12) washing the filter twice with 10 ml portions of the sodium acetate solution (4.5.5) each time.