INTERNATIONAL STANDARD 334

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Coal and coke — Determination of total sulphur — Eschka method

Charbon et coke — Dosage du soufre total — Méthode Eschka

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Coal and coke — Determination of total sulphur — Eschka method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a method of determining the total sulphur content of hard coal, brown coal, lignite and coke by the Eschka method. An alternative method for the determination of total sulphur is given in ISO 351.[1)]

2 PRINCIPLE

The sample of coal or coke 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.

3 REAGENTS

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

3.1 FOR BOTH METHODS

3.1.1 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 shall entirely pass a test sieve of 0,2 mm aperture.

3.1.2 Hydrochloric acid, ρ 1,18 g/ml.

3.1.3 Standard sulphate solution

Dissolve 0,600 0 g of potassium sulphate in water and dilute to 1 000 ml.

10 ml of this solution corresponds to :

0,008 0 g of barium sulphate or

1,033 ml of 0,1 N sodium thiosulphate solution.

3.2 FOR THE GRAVIMETRIC METHOD

3.2.1 Barium chloride, 85 g/ml solution.

Dissolve 100 g of barium chloride dihydrate in water and dilute to 1 l. Filter the solution through a fine-textured doubly acid-washed paper.

3.2.2 Methyl red indicator solution

Dissolve 1 g of 4′-dimethylaminoazobenzene-2-carboxylic acid (methyl red) in 600 ml of ethanol or industrial spirit and dilute to 1 l with water.

3.3 FOR THE GRAVIMETRIC ACID-EXTRACTION METHOD

3.3.1 Ammonia solution, ρ 0,88 g/ml, or the nearest obtainable.

3.4 FOR THE GRAVIMETRIC AQUEOUS-EXTRACTION METHOD AND THE TITRIMETRIC METHOD

3.4.1 Hydrogen peroxide, 300 g/l solution ("100 volumes").

3.5 FOR THE TITRIMETRIC METHOD

3.5.1 Potassium iodide.

3.5.2 Sodium hydroxide, 80 g/l solution.

Dissolve 80 g of sodium hydroxide in water and dilute to 1 l.

3.5.3 Barium chromate, 30 g/l solution.

To 30 g of barium chromate add 100 ml of water and 100 ml of perchloric acid (ρ 1,54 g/ml) and warm until

1) ISO 351, *Coal and coke — Determination of total sulphur — High temperature combustion method.*

solution is complete. Dilute the solution to 1 l and filter into a storage bottle through a fine-textured, doubly acid-washed filter paper or a filter paper pad. Store overnight before using.

The solution prepared from commercially available barium chromate shall be tested for suitability. This is done by using it to carry out duplicate determinations, by the method described in clause 6, 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 shall 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 min, filter by suction through a fine-textured, doubly 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 l beaker, add 200 ml of distilled water and 100 ml of perchloric acid (ρ 1,54 g/ml) and warm until solution is complete. Dilute the solution to 1 l with water and filter into a storage bottle through a fine-textured, doubly acid-washed filter paper or a filter paper pad.

3.5.4 Sodium acetate, 136 g/l solution.

Dissolve either 136 g of anhydrous sodium acetate or 225 g of the trihydrate in water and dilute to 1 l.

3.5.5 Sodium acetate, 9 g/l solution.

Dissolve either 9 g of anhydrous sodium acetate or 15 g of the trihydrate in water and dilute to 1 l.

3.5.6 Diluted ammonia solution

Dilute the ammonia solution (3.3.1) with an equal volume of water; dilute other strengths appropriately. Store this solution over calcium oxide to remove carbonate.

3.5.7 Sodium thiosulphate, approximately 0,1 N solution.

Dissolve 25 g of sodium thiosulphate pentahydrate in freshly boiled water, add 1 ml chloroform and dilute to 1 000 ml with water. Standardize this solution before use against 0,1 N potassium iodate in the presence of a trace of potassium iodide.

3.5.8 Mixed indicator solution

Solution A

Dissolve 0,125 g of 4′-dimethylaminoazobenzene-2-carboxylic acid (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. Discard the mixed solution after 1 week.

3.5.9 Phenol red indicator solution

Grind 1 g of phenol-sulphonphthalein (phenol red) with 28,4 ml of 0,4 % sodium hydroxide solution and dilute to 1 l.

3.5.10 Starch indicator, 10 g/l solution.

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 min and cool. Prepare fresh daily.

4 APPARATUS

All graduated apparatus shall be of the best analytical quality obtainable and the balance used shall be sensitive to 0,1 mg.

4.1 FOR BOTH METHODS

4.1.1 Electrically heated muffle furnace[1], with a zone of substantially uniform temperature at 800 ± 25 °C and a ventilation rate of 4 to 6 air changes per minute.

NOTE — The necessary rate of air change is obtained by using a suitably designed furnace, and may be checked by means of a pitot-static tube.

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

4.2 FOR THE GRAVIMETRIC METHOD

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

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

1) 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.

5 PREPARATION OF SAMPLE

The coal or coke used for the determination of total sulphur content is the analysis sample ground to pass a sieve of 0,2 mm aperture. If necessary, the sample is exposed in a thin layer for the minimum time required for the moisture content to reach approximate equilibrium with the laboratory atmosphere.

Before commencing the determination, mix the air-dried sample of coal or coke for at least 1 min, preferably by mechanical means.

6 PROCEDURE

6.1 Amount of sample

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

Sample mass	Range of total sulphur content	
	Gravimetric method	Titrimetric method
g	%	%
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

For coke, a 1 g sample is required.

6.2 Preparation of solution

6.2.1 *Coal sample*

Cover the bottom of the 25 ml crucible uniformly with 0,5 g of the Eschka mixture (3.1.1). Weigh accurately 1 g, 0,5 g, 0,25 g or 0,1 g of the coal sample (according to the expected sulphur content and the method of determination) and mix it intimately with 2,5 g of the Eschka mixture 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.

NOTE – Weigh out the total of 4 g of the Eschka mixture and extract from this the 0,5 and 1 g portions required for the bottom and top layers. It is convenient for this purpose to calibrate a small glass tube for each batch of Eschka mixture to deliver 0,5 g and 1 g without weighing. The bottom layer of Eschka mixture below the coal or coke mixture reduces attack on the porcelain surface, so that the extraction of sulphate with hot water is complete even when the surface deteriorates.

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 h, maintaining this temperature for a further 1 1/2 h. Withdraw the crucible (or crucibles) and allow to cool.

NOTE – The cracking of porcelain crucibles is prevented if they are slowly cooled by insertion in supports of light porous firebrick on removal from the muffle.

6.2.2 *Coke sample*

Cover the bottom of the 25 ml crucible uniformly with 0,5 g of the Eschka mixture (3.1.1). Weigh accurately 1 g of the coke sample and mix it intimately with 2,5 g of the Eschka mixture 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.

NOTE – Weigh out the total of 4 g of the Eschka mixture and extract from this the 0,5 and 1 g portions required for the bottom and top layers. It is convenient for this purpose to calibrate a small glass tube for each batch of Eschka mixture to deliver 0,5 g and 1 g without weighing. The bottom layer of Eschka mixture below the coal or coke mixture reduces attack on the porcelain surface, so that the extraction of sulphate with hot water is complete even when the surface deteriorates.

Place the charged crucible (or crucibles) on the cold insulating plate and insert into the muffle at a temperature of 800 ± 25 °C, maintaining this temperature for a further 1 1/2 h. Withdraw the crucible (or crucibles) and allow to cool.

NOTE – The cracking of porcelain crucibles is prevented if they are slowly cooled by insertion in supports of light porous firebrick on removal from the muffle.

6.2.3 *All samples*

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 in 6.3 and 6.4.

6.3 Gravimetric method

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

Acid extraction, see 6.3.1.

Aqueous extraction, see 6.3.2.

6.3.1 *Acid extraction*

Place a cover glass on the beaker and then carefully add sufficient of the hydrochloric acid (3.1.2) – 17 ml will normally be required – to dissolve the solid matter, warming the contents of the beaker to effect solution. Boil for 5 min to expel carbon dioxide and filter, collecting the filtrate in a 400 ml conical beaker.

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

To prepare the filter paper pad, shake doubly 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.