
INTERNATIONAL STANDARD



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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

Coal and coke — Determination of total sulphur — Eschka method

Charbon et coke — Dosage du soufre total — Méthode Eschka

First edition — 1975-01-15

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 334:1975

<https://standards.iteh.ai/catalog/standards/sist/6c05bfc4-eb28-474f-ad21-a0a1c72bc979/iso-334-1975>

UDC 662.66 : 662.749.2 : 543.845

Ref. No. ISO 334-1975 (E)

Descriptors : coal, chemical analysis, determination of content, sulphur, gravimetric analysis, volumetric analysis.

Price based on 5 pages

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 furnace¹⁾, 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 cm² area, with distilled water in a bottle until the paper is thoroughly disintegrated.

Place a perforated 25 mm diameter porcelain plate in a 75 mm funnel, close the stem of the funnel with a finger and add water until the plate is immersed and the funnel stem is full. Shake on to the plate sufficient paper 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 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.

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 (3.2.2) and then, cautiously, add the ammonia solution (3.3.1) until the colour of the indicator changes and a trace of precipitate is formed. Add sufficient of the hydrochloric acid (3.1.2) to just redissolve the precipitate and then add 1 ml in excess.

6.3.2 Aqueous extraction

Add to the contents of the beaker 1 ml of the hydrogen peroxide (3.4.1). Heat at 80 °C for 30 min 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 cm² area, with distilled water in a bottle until the paper is thoroughly disintegrated.

Place a perforated 25 mm diameter porcelain plate in a 75 mm funnel, close the stem of the funnel with a finger and add water until the plate is immersed and the funnel stem is full. Shake on to the plate sufficient paper 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 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.

Wash the filter with five 20 ml portions of hot water.

Boil to remove hydrogen peroxide, using methyl red (3.2.2) to indicate completeness of removal. Add the hydrochloric acid (3.1.2) drop by drop until the colour changes to red and then add 1 ml in excess. Boil for 5 min 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 (3.2.1) from a pipette with a delivery time of approximately 20 s, 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 min.

NOTE — It has been shown that complete recovery of the barium sulphate can be made by filtering after 30 min 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 standing time of 30 min.

Filter, using one of the following techniques :

- 1) By gravity, through an ashless, fine-textured, doubly acid-washed paper in a fluted, long-stemmed 60° funnel;
- 2) By gravity, through a filter paper pad prepared from ashless, doubly acid-washed paper (see note 6.3.1);

- 3) By suction, using asbestos in a Gooch crucible which has been previously dried for 1 h at a temperature of 130 ± 10 °C and weighed.

NOTE — Rapid filtration is obtained by each of the techniques, 1), 2) and 3). The following precautions should be observed :

- a) A filter circle should be carefully folded to fit the funnel so that the stem remains full of liquid.
- b) After transferring the filter paper pad to the crucible, wipe the funnel successively with two halves of a circle of ashless filter paper, which are then incinerated with the pad.
- c) The Gooch crucible should be used with specially prepared filtration asbestos.

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 min at 800 ± 25 °C.

NOTE — Under these conditions ignition of the wet filter paper is achieved rapidly; mechanical loss is avoided by the use of an insulating plate.

If a Gooch crucible is used (technique 3)), dry previously for 1 h at 130 ± 10 °C, then allow to cool and weigh.

6.3.3 Blank determination

Carry out a blank determination under the same conditions, but omitting the sample. Add 10 ml of the standard sulphate solution (3.1.3) to the filtrate before adding the methyl red indicator solution (3.2.2). 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.

6.4 Titrimetric method

6.4.1 Treatment of solution

Add to the contents of the beaker 1 ml of the hydrogen peroxide (3.4.1). Heat at 80 °C for 30 min and filter, collecting the filtrate in a 400 ml conical beaker (see note, 6.3.1). Wash the filter five times with 20 ml portions of hot water each time.

Boil the combined filtrate and washings for 10 min. Add 2 or 3 drops of the mixed indicator solution (3.5.8) or the phenol red indicator solution (3.5.9) and acidify by the careful addition of 5 ml of the hydrochloric acid (3.1.2). Boil the solution until the volume is reduced to between 80 and 100 ml. While still hot, add the sodium hydroxide solution (3.5.2) drop by drop, until the solution is just alkaline.

Add 10 ml of the barium chromate solution (3.5.3) drop by drop, from a pipette, to the hot solution, stirring during the addition, and boil for 2 or 3 min. Add 10 ml of the sodium acetate solution (3.5.4). Boil for 2 or 3 min, then carefully add the ammonia solution (3.5.6) 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 min.

Filter the cool solution into a 400 ml conical beaker or flask (see note 6.3.2) washing the filter twice with 10 ml portions of the sodium acetate solution (3.5.5) each time.

Add 1 to 2 g of the potassium iodide (3.5.1) to the filtrate, dissolve by swirling the vessel and add 5 ml of the hydrochloric acid (3.1.2). Allow to stand for 5 min and titrate the liberated iodine with the sodium thiosulphate solution (3.5.7), using the starch indicator solution (3.5.10).

6.4.2 Blank determination

Carry out a blank determination under the same conditions, but omitting the sample. Add 10 ml of the standard sulphate solution (3.1.3) to the filtrate before adding the methyl red indicator solution (3.2.2). The mass of the sulphur found in the blank determination, less the equivalent of the standard sulphate solution added, is deducted from that obtained in the full determination.

7 EXPRESSION OF RESULTS

7.1 Gravimetric method

The sulphur content (S), of the sample as analysed¹⁾, expressed as a percentage by mass, is given by the formula

$$S = \frac{13,74 (m_2 - m_3 + 0,008 0)}{m_1}$$

where

- m_1 is the mass of sample taken, in grams;
- m_2 is the mass of barium sulphate found in the determination, in grams;
- m_3 is the mass of barium sulphate found in the blank determination, in grams.

The result (preferably the mean of duplicate determinations, see clause 8) shall be reported to the nearest 0,1 %.

7.2 Titrimetric method

The sulphur content (S), of the sample as analysed¹⁾, expressed as a percentage by mass, is given by the formula

$$S = \frac{1,069 T (V_1 - V_2 + \frac{1,033}{T})}{m} = \frac{1,069 T (V_1 - V_2) + 1,014}{m}$$

where

- m is the mass of sample taken, in grams;
- V_1 is the volume of sodium thiosulphate solution required in the full determination, in millilitres;
- V_2 is the volume of sodium thiosulphate solution required in the blank determination, in millilitres;
- T is the normality of the sodium thiosulphate solution (i.e. 0,100 0, if the solution is exactly decinormal).

The result (preferably the mean of duplicate determinations, see clause 8) shall be reported to the nearest 0,1 %.

8 PRECISION OF THE METHOD

		Maximum acceptable differences between results (calculated to the same moisture content)	
Sulphur	Same laboratory (Repeatability)	Different laboratories (Reproducibility)	
	0,05 % absolute	0,10 % absolute	

8.1 Repeatability

The results of duplicate determinations, carried out at different times, in the same laboratory, by the same operator with the same apparatus on the same analysis sample, shall not differ by more than the above value.

8.2 Reproducibility

The means of the results of duplicate determinations, carried out in each of two laboratories on representative portions taken from the same sample after the last stage of sample preparation, shall not differ by more than the above value.

9 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.

1) Calculation of the results to other bases is dealt with in ISO/R 1170.