INTERNATIONAL STANDARD ISO 157

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Hard coal – Determination of forms of sulphur

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up has the right to be represented on that Committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the Technical Committees are circulated to the Member Bodies for approval before their acceptance as International Standards by the ISO Council.

Prior to 1972, the results of the work of the Technical Committees were published as ISO Recommendations; these documents are now in the process of being transformed into International Standards. As part of this process, Technical Committee ISO/TC 27 has reviewed ISO Recommendation R 157 and found it technically suitable for transformation. International Standard ISO 157 therefore replaces ISO Recommendation R 157-1960 to which it is technically identical.

ISO Recommendation R 157 was approved by the Member Bodies of the following countries :

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The Member Body of the following country expressed disapproval of the Recommendation on technical grounds :

France

No Member Body disapproved the transformation of ISO/R 157 into an International Standard.

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INTERNATIONAL STANDARD

ISO 157-1975 (E)

Hard coal – Determination of forms of sulphur

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies methods of determining the sulphate sulphur and pyritic sulphur contents of hard coal and of calculating the amount of organic sulphur present.

2 PRINCIPLE

2.1 General

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.

2.2 Sulphate sulphur

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

either gravimetrically, see clause 4;

or titrimetrically, see clause 5.

2.3 Pyritic sulphur

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 clause 6.

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 clause 7.

2.4 Organic sulphur

Organic sulphur is calculated by deducting the sum of percentages of "sulphate" and "pyritic" sulphur from the total sulphur in the coal, see clause 8.

2.5 Calculation to other bases

The results of these determinations are reported on the "air-dried" basis; calculation of the results to other bases is dealt with in ISO/R 1170.

3 PREPARATION OF SAMPLE

The coal used for the determination of sulphate sulphur and pyritic sulphur is the analysis sample ground to pass a sieve of 0,2 mm aperture. If necessary expose the sample 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 thoroughly for at least 1 min, preferably by mechanical means.

4 SULPHATE SULPHUR – GRAVIMETRIC METHOD

4.1 Reagents

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

4.1.1 Hydrochloric acid, ρ 1,18 g/ml.

4.1.2 Hydrochloric acid.

Dilute 420 ml of the hydrochloric acid (4.1.1) to 1 l with water.

4.1.3 Hydrochloric acid.

Dilute 42 ml of the hydrochloric acid (4.1.1) to 1 l with water.

4.1.4 Barium chloride, 85 g/l solution

Dissolve 100 g of barium chloride dihydrate in water and dilute to 1 l. Filter before use through a close-textured, doubly acid-washed filter paper or filter paper pad.

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

4.1.6 Bromine water.

Prepare a saturated solution of bromine in water.

4.1.7 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 $\triangleq$ 0,008 0 g of $BaSO_4$.

4.1.8 Methyl orange indicator solution.

Dissolve 0,5 g of dimethyl-amino-azobenzene-sulphonic acid (methyl orange) in 1 l of water; filter the cold solution if a precipitate separates.

4.2 Apparatus

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

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

or

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

4.2.3 Cold finger condenser (see figure 1).

4.3 Procedure

Weigh accurately about 5 g of the sample, transfer to a 250 ml conical flask, add 50 ml of the hydrochloric acid (4.1.2) and fit a cold finger condenser (4.2.3) into the neck of the flask. Boil for 30 min and filter through a medium-textured, doubly acid-washed paper. Wash six times with the hydrochloric acid (4.1.3), using a total quantity of about 20 ml. Discard the residual coal.

Add 1 ml of the bromine water (4.1.6) to the filtrate and boil for 5 min to ensure that all the iron is in the ferric state. Precipitate the iron by adding the ammonia solution (4.1.5) 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 6.3, last paragraph).

To the filtrate add 2 or 3 drops of the methyl orange indicator solution (4.1.8) and then, cautiously, add the hydrochloric acid (4.1.1) until the colour of the solution changes, then add 1 ml of acid in excess. The volume of the solution shall be between 150 and 250 ml.

Add 10,0 ml of the standard sulphate solution (4.1.7), 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 (4.1.4) 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, without agitation, for 30 min (see note 1).

Filter, using one of the following techniques (see note 2) :

1 By gravity through an ashless, close-textured, doubly acid-washed filter paper of 100 to 125 mm diameter in a fluted, long-stemmed 60° funnel, or

2 By gravity through a filter paper pad prepared from ashless, doubly acid-washed paper, or

3 Under suction, using asbestos in a Gooch crucible, previously dried for 1 h at 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, porcelain or platinum capsule on the silica plate and insert into the muffle furnace for 15 min at 800 ± 25 °C (see note 3), then allow to cool and weigh. If a Gooch crucible is used (technique 3), dry for 1 h at 130 ± 10 °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 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 30 min standing time mentioned above.

2 Filtration of the precipitate. Rapid filtration is obtained by any of the techniques 1, 2 or 3, indicated in 4.3.

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

Technique 2 : 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.

Place a 25 mm porcelain filter cone in a 75 mm 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; mechanical loss is avoided by the use of a thick insulating plate.

4.4 Blank determination

Carry out a blank determination under the same conditions, but omitting the coal. Add 10,0 ml of the standard sulphate solution (4.1.7) to the filtrate before adding the methyl orange indicator solution (4.1.8). 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.

4.5 Expression of results

The sulphate sulphur content (S_s) of the sample as analysed, expressed as a percentage by mass, is given by the formula

$$S_s = \frac{13{,}74\,(m_2 - m_3)}{m_1}$$

where

m_1 is the mass of sample taken, in grams;

m_2 is the mass of barium sulphate found in the full 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 4.6) shall be reported to the nearest 0,1 %.

4.6 Precision of the method

Sulphate sulphur	Maximum acceptable difference between results (calculated to the same moisture content)	
	Same laboratory (Repeatability)	Different laboratories (Reproducibility)
	0,02 % absolute	0,03 % absolute

4.6.1 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.

4.6.2 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.

5 SULPHATE SULPHUR – TITRIMETRIC FINISH

5.1 Reagents

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

5.1.1 Cation exchange resin[1] of analytical reagent quality, 0,5 to 1,5 mm.

5.1.2 Potassium iodide.

5.1.3 Hydrochloric acid, ρ 1,18 g/ml.

5.1.4 Hydrochloric acid.

Dilute 420 ml of the hydrochloric acid (5.1.3) to 1 l with water.

5.1.5 Hydrochloric acid.

Dilute 42 ml of the hydrochloric acid (5.1.3) to 1 l with water.

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

5.1.7 Sodium hydroxide, 80 g/l solution.

Dissolve 80 g of sodium hydroxide in 1 l of water.

5.1.8 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 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 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 5.3, 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 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 water until the last 20 ml of the washings give no more than a faint trace of opalescence with silver nitrate solution.

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[1] Suitable resins are known as Amberlite IR-120 (H) and Lewatit 22.

Wash the precipitate by means of a jet of water into a 2 l beaker, add 200 ml of 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 filter paper pad.

5.1.9 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.

5.1.10 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.

5.1.11 Ammonia solution.

Dilute ammonia solution (ρ 0,88 g/ml or nearest obtainable) with an equal volume of water. Store this solution over calcium oxide to remove carbonate.

5.1.12 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 ≙ 1,033 ml of 0,1 N sodium thiosulphate solution (5.1.13).

5.1.13 Sodium thiosulphate, approximately 0,1 N solution.

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 potassium iodate in the presence of a trace of potassium iodide.

5.1.14 Mixed indicator solution.

Solution A — Dissolve 0,125 g of 4′-dimethylamino-azobenzene-2-carboxylic acid (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-bisdimethylamino-phenazothionium chloride (methylene blue) in 100 ml of ethanol or industrial methylated spirit. Store in a dark glass bottle.

Mix equal volumes of solutions A and B. Discard the mixed solution after 1 week.

5.1.15 Phenol red indicator solution.

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

5.1.16 Starch indicator, 1 g/l solution.

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 min and cool. Prepare fresh daily.

5.2 Apparatus

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

5.2.1 Cation exchanger. The glass column is 200 ± 20 mm long, internal diameter 20 to 25 mm, and contains 35 ± 5 g of cation exchange resin. The column outlet is restricted with either a sintered glass disk or an S-shaped capillary of 2 to 3 mm internal diameter. The linear flow rate should be adjusted to approximately 40 mm/min.

5.3 Procedure

Weigh accurately about 5 g of the sample, transfer to a 250 ml conical flask, add 50 ml of the hydrochloric acid (5.1.4) and fit a cold finger condenser (4.2.3) into the neck of the flask. Boil for 30 min and filter through a medium-textured, doubly acid-washed paper. Wash six times with the dilute hydrochloric acid (5.1.5) using a total quantity of about 20 ml. Discard the residual coal.

Add 1 drop of the hydrogen peroxide (5.1.6) to the filtrate and evaporate to dryness. Moisten the residue with the hydrochloric acid (5.1.3), add 30 ml of water, boil and filter through the cation exchanger; wash with 60 to 70 ml of water. Add to the solution and washings, by means of a pipette, 10,0 ml of the standard sulphate solution (5.1.12) and boil the solution. While still hot, add 2 or 3 drops of the mixed indicator solution (5.1.14) or the phenol red indicator solution (5.1.15), then add the sodium hydroxide solution (5.1.7) drop by drop until the solution is just alkaline.

To the hot solution add 10 ml of the barium chromate solution (5.1.8) drop by drop from a pipette, stirring during the addition, and boil for 2 to 3 min, then add 10 ml of the sodium acetate solution (5.1.9). Boil for a further 2 to 3 min, then carefully add the ammonia solution (5.1.11) until the solution is distinctly alkaline; continue boiling until the excess ammonia is expelled, then allow to cool for 20 min.

Filter the cool solution into a 400 ml conical beaker or conical flask, using one of the following methods (see note) :

1) by gravity through an ashless, close-textured, doubly acid-washed filter paper of 100 to 125 mm diameter in a fluted, long-stemmed 60° funnel, or

2) under suction, using asbestos in a Gooch crucible.

Wash the filter twice, using each time a 10 ml portion of the sodium acetate solution (5.1.10).

Add 1 to 2 g of the potassium iodide (5.1.2) to the filtrate, dissolve by swirling the vessel, then add 5 ml of the hydrochloric acid (5.1.3). Allow to stand for 5 min and titrate the liberated iodine with the sodium thiosulphate solution (5.1.13), using the starch indicator solution (5.1.16).

NOTE — Rapid filtration is obtained by either of the two techniques given below :

1) a filter circle should be carefully folded to fit the funnel so that the stem remains full of liquid.

2) the Gooch crucible should be used with specially prepared filtration asbestos.

5.4 Blank determination

Carry out a blank determination under the same conditions, but omitting the coal.

5.5 Expression of results

The sulphate sulphur content (S_s) of the sample as analysed, expressed as a percentage by mass, is given by the formula

$$S_s = \frac{1,069\, N\, (V_1 - V_2)}{m}$$

where

m is the mass of sample taken, in grams;

V_1 is the volume of sodium thiosulphate required in the full determination, in millilitres;

V_2 is the volume of sodium thiosulphate required in the blank determination, in millilitres;

N 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 5.6) shall be reported to the nearest 0,1 %.

5.6 Precision of the method

	Maximum acceptable differences between results (calculated to the same moisture content)	
	Same laboratory (Repeatability)	Different laboratories (Reproducibility)
Sulphate sulphur	0,02 % absolute	0,03 % absolute

5.6.1 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.

5.6.2 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.

6 PYRITIC SULPHUR – OXIDATION METHOD

6.1 Reagents

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

6.1.1 Nitric acid.

Dilute 125 ml of nitric acid (ρ 1,42 g/ml) to 1 l with water.

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

6.1.3 Hydrochloric acid.

Dilute 420 ml of hydrochloric acid (ρ 1,18 g/ml) to 1 l with water.

6.1.4 Sulphuric-phosphoric acid mixture.

Carefully mix 150 ml of sulphuric acid (ρ 1,84 g/ml) and 150 ml of phosphoric acid (ρ 1,75 g/ml). Add this to 600 ml of water, cool and dilute to 1 l.

6.1.5 Tin(II) chloride, 50 g/l solution.

Dissolve 5 g of anhydrous tin(II) chloride or 6 g of the dihydrate in 50 ml of hydrochloric acid (ρ 1,18 g/ml) and add this solution to 50 ml of water.

Prepare this solution freshly before use.

6.1.6 Mercury(II) chloride, 60 g/l solution.

Add 6 g of mercury(II) chloride to 100 ml of water and shake the mixture for 10 min.

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

6.1.8 Potassium dichromate, 0,017 9 N solution.

Dissolve 0,878 0 g of potassium dichromate in water and dilute to 1 000 ml.

6.1.9 Sodium diphenylamine sulphonate indicator, 2 g/l solution.

Dissolve 0,2 g of sodium diphenylamine sulphonate in water and dilute to 100 ml. Store in a dark bottle.

6.2 Apparatus

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

6.3 Procedure

Weigh accurately about 1 g of the sample, transfer to a conical flask, add 50 ml of the nitric acid (6.1.1) and fit a cold finger condenser (4.2.3) into the neck of the flask. Boil for 30 min and filter through a medium-textured, doubly acid-washed paper. Wash six times with the nitric acid (6.1.1).

Add 2 ml of the hydrogen peroxide (6.1.2) to the filtrate and boil for 5 min to destroy any coloration arising from the decomposition of the coal.

Precipitate the iron by adding the ammonia solution (6.1.7) in a slow stream to the boiling solution until a slight excess is present and then add 5 ml in excess. Filter on a fast toughened filter paper and wash the precipitate with hot water. Pierce the filter paper and wash the precipitate with a fine jet of hot water into a 500 ml conical flask or conical beaker. Pour 10 ml of the hydrochloric acid (6.1.3) on the filter in small portions to remove the last traces of iron and give a final wash with hot water. If necessary, warm the solution to dissolve the iron hydroxide. The total volume shall not exceed 20 ml by any considerable amount; if necessary, reduce the volume by evaporation before proceeding.

Heat to boiling and add the tin(II) chloride solution (6.1.5) drop by drop, from a pipette or dropping bottle, stirring until the yellow colour disappears. Add 5 drops in excess, cool to room temperature and rapidly add 10 ml of the mercury(II) chloride solution (6.1.6); a silky precipitate of mercury(I) chloride is formed.

Add 15 ml of the sulphuric-phosphoric acid mixture (6.1.4), dilute to between 150 and 200 ml with water, add 5 drops of the indicator solution (6.1.9) and titrate with the potassium dichromate solution (6.1.8). Near the end point, the colour of the solution deepens to blue-green or, in the presence of a large amount of iron, to greenish-blue. Add the dichromate drop by drop until the colour changes to an intense violet-blue. The titration gives a measure of the total iron of the sample.

Determine the non-pyritic iron, by the method described above, in the precipitate A reserved for this purpose in 4.3.

6.4 Expression of results

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

$$S_p = 0{,}115 \left(\frac{V_1}{m_1} - \frac{V_2}{m_2} \right)$$

where

V_1 is the volume, in millilitres, of potassium dichromate solution equivalent to the total iron in a sample of mass m_1, in grams;

V_2 is the volume, in millilitres, of potassium dichromate solution equivalent to the non-pyritic iron in a sample of mass m_2, in grams.

The result (preferably the mean of duplicate determinations, see 6.5) shall be reported to the nearest 0,1 %.

6.5 Precision of the method

Pyritic sulphur	Maximum acceptable difference between results (calculated to the same moisture content)	
	Same laboratory (Repeatability)	Different laboratories (Reproducibility)
less than 0,5 %	0,05 % absolute	0,10 % absolute
0,5 % up to 1,5 %	0,07 % absolute	0,15 % absolute
over 1,5 %	5 % of the result	10 % of the result

6.5.1 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.

6.5.2 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.

7 PYRITIC SULPHUR – REDUCTION METHOD

7.1 Reagents

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

7.1.1 Sodium carbonate, anhydrous.

7.1.2 Chromium metal, powdered.

7.1.3 Zinc metal, granulated.

7.1.4 Ethanol, 95 % (V/V).

7.1.5 Hydrochloric acid, ρ 1,18 g/ml.

7.1.6 Hydrochloric acid.

Dilute 525 ml of the hydrochloric acid (7.1.5) to 1 l with water.

7.1.7 Acetic acid, glacial, ρ 1,05 g/ml.

7.1.8 Cadmium acetate, 43 g/l solution.

Dissolve 50 g of cadmium acetate dihydrate in water, add 10 ml of glacial acetic acid (7.1.7) and dilute to 1 l with water.

7.1.9 Sodium thiosulphate, approximately 0,1 N solution.

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 the potassium iodide-iodate solution (7.1.11).

7.1.10 Iodine, approximately 0,1 N solution.

Dissolve about 12,7 g of iodine in a solution containing 25 g of potassium iodide in about 35 ml of water. When all the iodine has dissolved, dilute to 1 000 ml with water. Standardize this solution with the sodium thiosulphate solution (7.1.9).

7.1.11 Potassium iodide-iodate, 0,031 25 N solution with respect to potassium iodate.

Dissolve 1,114 6 g of potassium iodate and 10 g of potassium iodide in water and dilute to 1 000 ml with water.

7.1.12 Starch indicator, 10 g/l solution.

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 min and cool. Prepare fresh daily.

7.2 Apparatus

All graduated apparatus shall be of the best analytical quality obtainable, and the balance used shall be sensitive to 0,1 mg. The apparatus shall consist of the following (see figure 2) :

7.2.1 Reaction flask, round-bottomed, of about 100 ml capacity, with a wide neck fitted with a standard conical ground glass socket.

7.2.2 A "head", consisting of a wide glass tube with at its lower end a ground glass cone to fit the socket of the flask and at its upper end :

a) a dropping funnel fused into position in line with the axis of the tube,

b) a gas off-take tube.

The function of the centre piece is to act as a splash guard and to prevent carry-over of acid mist.

7.2.3 Mercury safety trap.

7.2.4 Wash bottle, containing distilled water for the absorption of hydrochloric acid gas.

7.2.5 Two wash bottles, containing cadmium acetate solution for the absorption of the hydrogen sulphide produced.

7.2.6 Cylinder, containing compressed carbon dioxide.

7.3 Procedure

Grind 5 to 10 g of the sample until the particle size is such that at least 95 % is smaller than 0,02 mm (see note 1). Mix well.

Weigh, then transfer 0,500 g of the finely ground coal sample to the reaction flask of the apparatus as shown in figure 2, taking precautions to avoid the re-absorption of moisture by the dry coal during the operation of weighing. Add 3 to 5 ml of the ethanol (7.1.4), 15 g of the zinc (7.1.3) and 0,1 g of the chromium (7.1.2) and shake the contents of the flask until a paste is formed. Fit the flask to the remainder of the apparatus and charge the dropping funnel (connected to the cylinder of carbon dioxide) with 70 ml of the hydrochloric acid (7.1.5), to which 3 ml of the ethanol (7.1.4) have been added. Admit about 5 ml of acid to the reaction flask to allow the formation of Cr^{2+} and then, in successive portions, the remainder, over a period of 10 min. When the evolution of hydrogen ceases, after a further 15 to 20 min, pass a current of carbon dioxide to purge all hydrogen sulphide from the apparatus into the cadmium acetate absorbers (see note 2).

Add to the absorber containing the precipitate of cadmium sulphide (see note 3) a measured volume in sufficient excess of either the iodine solution (7.1.10) or the potassium iodide-iodate solution (7.1.11), add 20 ml of the hydrochloric acid (7.1.6) and agitate until the precipitate is dissolved. Transfer the contents of the absorber into a conical beaker or flask, then rinse the absorber with water and add the washings to the beaker or flask; add the starch indicator solution (7.1.12) and titrate the excess iodine with the sodium thiosulphate solution (7.1.9).

NOTES

1 The reduction in particle size of the sample can be achieved in one of the following ways :

a) Mechanical grinding. Grind the sample mechanically with 5 ml of ethanol (7.1.4) for 30 min in a steel tube, 150 mm long and 20 mm in internal diameter, which is half filled with steel balls of 5 mm in diameter and is closed at both ends with rubber stoppers; or

Rotate the sample with 5 ml of ethanol (7.1.4) for 30 min in a cylindrical bronze cup, 75 mm in internal diameter and 55 mm deep, which contains 80 steel balls of 5 to 6 mm in diameter and into which two leaf springs are arranged to project downwards in order to stir the contents, fixed to a shaft inclined at 30° to the vertical and making 100 rev/min (see figure 3).

In either case, transfer the contents of the apparatus to a porcelain dish, dry for 30 min at 105 °C in an atmosphere of oxygen-free nitrogen, separate the steel balls, pulverize the caked dried coal and transfer it to a stoppered weighing bottle to prevent re-absorption of moisture.

b) Hand grinding. Alternatively, the required particle size can be obtained by careful grinding of 0,500 g of coal in an agate mortar with repeated additions of a small quantity of ethanol. Thereafter the pulverized coal is transferred quantitatively into the reaction flask.

2 The second absorber containing cadmium acetate solution is necessary because large quantities of hydrogen sulphide may not all be absorbed in the first absorber.

3 Should there be a turbidity in the solution contained in the second absorber, combine its contents with those of the first cadmium acetate absorber before adding the iodine solution.