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ISO RECOMMENDATION
R 157

DETERMINATION OF FORMS OF SULPHUR IN COAL

1st EDITION

June 1960

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BRIEF HISTORY

The ISO Recommendation R 157, *Determination of Forms of Sulphur in Coal*, 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 the second meeting of the Technical Committee, held in London, in December 1951, the question of the determination of forms of sulphur in coal was discussed for the first time, and in July 1952, a draft proposal was circulated.

At the third meeting of ISO/TC 27, held in London, in November 1953, a second draft proposal, modified in line with the comments received, was submitted to the Technical Committee, together with a possible alternative method based on comments from Germany, but there was not enough time to discuss them adequately. The members of the Committee were asked to send in their comments in writing, and the subject was also taken up by Working Groupe No. 3, *Sulphur*. At the latter's first meeting, in May 1954, it was agreed, after practical demonstrations, that the reduction method could be regarded as a satisfactory alternative to the oxydation method for the determination of pyritic sulphur.

A third draft proposal was worked out and discussed at the second metting of Working Group No. 3, in October 1954, before being circulated to the members of ISO/TC 27 in January 1955. This draft, which contained alternative methods for sulfate sulphur (gravimetric and titrimetric) and alternative methods for pyritic sulphur (oxidation and reduction), was examined, together with a report on the experimental work on which was based, at the fourth meeting of ISO/TC 27, held in Stockholm in June 1955. It was decided—with a reservation by France, which would have preferred to see only one method standardized, to use the third draft proposal as the basis for setting up a Draft ISO Recommendation for the determination of forms of sulphur.

This draft proposal was circulated in March 1956 to all the members of ISO/TC 27 for ratification and, with minor changes, was adopted as a Draft ISO Recommendation.

On 29 June 1957, the Draft ISO Recommendation (Nº 169) was distributed to all the ISO Member Bodies and was approved, subject to some modifications, by the following 24 (out of a total of 38) Member Bodies:

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

One Member Body opposed the approval of the Draft: France.

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 157 June 1960

DETERMINATION OF FORMS OF SULPHUR IN COAL

1. PRINCIPLE

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.

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

either gravimetrically, see section 2, Gravimetric Method,

or titrimetrically, see section 3, Titrimetric Method.

1.2 **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 section 4, Oxidation Method.

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 section 5, Reduction Method.

1.3 **Organic sulphur** is calculated by deducting the sum of percentages of "sulphate" and "pyritic" sulphur from the total sulphur in the coal, see section 6.

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2. SULPHATE SULPHUR — GRAVIMETRIC METHOD

2.1 Apparatus

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

2.1.1 *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

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

2.1.3 *Cold finger condenser* (see Fig. 1 below).

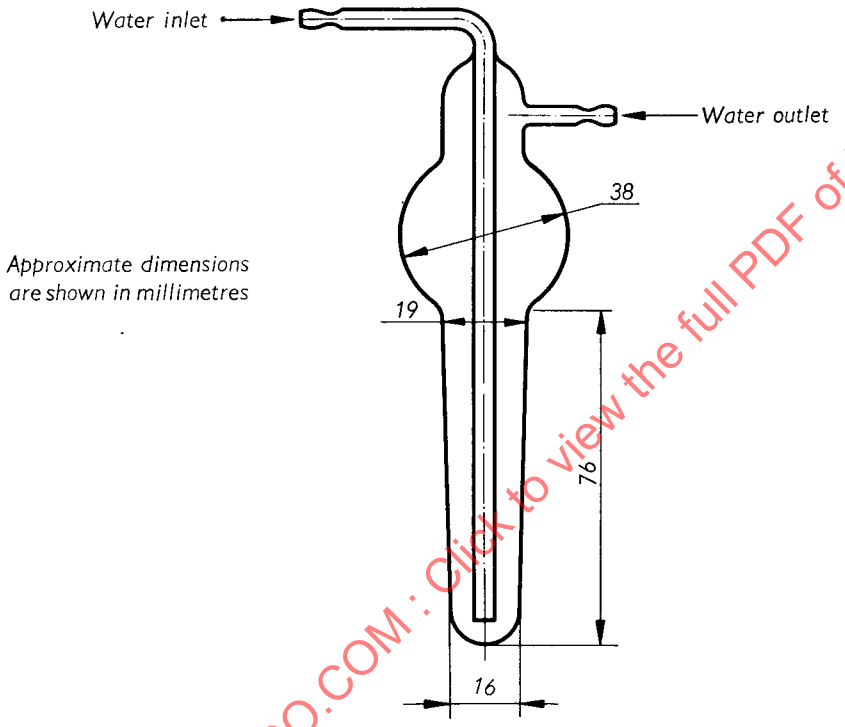

FIG. 1. — **Cold finger condenser for the determination of sulphate and pyritic sulphur**

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2.2 Reagents

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

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

2.2.2 *Hydrochloric acid.* Dilute 420 ml of the hydrochloric acid (2.2.1) to 1 litre with water.

2.2.3 *Hydrochloric acid.* Dilute 42 ml of the hydrochloric acid (2.2.1) to 1 litre with water.

2.2.4 *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 close-textured, double acid-washed filter paper or filter paper pad.

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

2.2.6 *Bromine water.* Prepare a saturated solution of bromine in water.

2.2.7 *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 = 0.008 0 g of $BaSO_4$.

2.2.8 *Methyl orange indicator solution.* Dissolve 0.5 g of dimethyl-amino-azobenzene-sulphonic acid (methyl orange) in 1 litre of water; filter the cold solution if a precipitate separates.

2.3 Procedure

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.

Weigh accurately about 5 g of the sample, transfer to a 250 ml conical flask, add 50 ml of the hydrochloric acid (2.2.2) and fit a cold finger condenser (see Fig. 1) into the neck of the flask. Boil for 30 minutes and filter through a medium-textured, double acid-washed paper. Wash 6 times with the hydrochloric acid (2.2.3), using a total quantity of about 20 ml. Discard the residual coal.

Add 1 ml of the bromine water (2.2.6) to the filtrate and boil for 5 minutes to ensure that all the iron is in the ferric state. Precipitate the iron by adding the ammonia solution (2.2.5) 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 clause 4.3, last paragraph).

To the filtrate add 2 or 3 drops of the methyl orange indicator solution (2.2.8) and then, cautiously, add the hydrochloric acid (2.2.1) until the colour of the solution changes, then add 1 ml of acid in excess. The volume of the solution should be between 150 and 250 ml.

Add 10.0 ml of the standard sulphate solution (2.2.7), 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 (2.2.4) 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, without agitation, for 30 minutes (see Note 1, page 6).

Filter, using one of the following techniques (see Note 2, page 6):

1. By gravity through an ashless, close-textured, double acid-washed filter paper of 10 to 12.5 cm diameter in a fluted, long-stemmed 60° funnel, or
2. By gravity through a filter paper pad prepared from ashless, double acid-washed paper, or
3. Under suction, using asbestos in a Gooch crucible, previously dried for 1 hour 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 minutes at 800 ± 25 °C (see Note 3, page 6), then allow to cool and weigh. If a Gooch crucible is used (technique 3), dry for 1 hour at 130 ± 10 °C, then allow to cool and weigh.

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NOTES

1. **Period of standing.** It has been shown that complete recovery of the barium sulphate can be made by filtering after 30 minutes 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 minutes standing time mentioned above.

2. **Filtration of the precipitate.** Rapid filtration is obtained by any of the techniques 1, 2 or 3, indicated in clause 2.3.

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

   Technique 2. 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.

   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, with mechanical loss is avoided by the use of a thick insulating plate.

2.3.1 *Blank determination.* Carry out a blank determination under the same conditions, but omitting the coal. Add 10.0 ml of the standard sulphate solution (2.2.7) to the filtrate before adding the methyl orange indicator solution (2.2.8). The weight of the barium sulphate found in the blank determination is deducted from that obtained in the full determination.

2.4 Calculation of results

If W = weight of sample, expressed in grammes,

a = weight of barium sulphate found in the full determination, expressed in grammes,

b = weight of barium sulphate found in the blank determination, expressed in grammes,

S_s = percentage of sulphate sulphur in the sample,

then

$$S_s = \frac{13.74\ (a - b)}{W}$$

2.5 Tolerances

The results of duplicate determinations carried out at different times in the same laboratory, on the same sample, by the same operator using the same apparatus, should not differ by more than 0.02 per cent of sulphate sulphur.

The means of the results of duplicate determinations carried out in different laboratories on representative samples taken from the same bulk after the last stage of reduction should not differ by more than 0.03 per cent of sulphate sulphur.

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3. SULPHATE SULPHUR — TITRIMETRIC FINISH

3.1 Apparatus

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

3.1.1 *Cation exchanger.* The glass column is 20 ± 2 cm long, internal diameter 2.0 to 2.5 cm, 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 4 cm/min.

3.2 Reagents

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

3.2.1 *Cation exchange resin** of analytical reagent quality, 0.5 to 1.5 mm.

3.2.2 *Potassium iodide.*

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

3.2.4 *Hydrochloric acid.* Dilute 420 ml of the hydrochloric acid (3.2.3) to 1 litre with water.

3.2.5 *Hydrochloric acid.* Dilute 42 ml of the hydrochloric acid (3.2.3) to 1 litre with water.

3.2.6 *Hydrogen peroxide*, 30 per cent (weight/volume) ("100 volumes").

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

3.2.8 *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 clause 3.3), 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 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.

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

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3.2.9 *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.

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

3.2.11 *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.

3.2.12 *Standard sulphate solution.* Dissolve 0.600 0 g of potassium sulphate in water and dilute to 1000 ml.
10 ml of standard sulphate solution = 1.033 ml of 0.1 N sodium thiosulphate solution (3.2.13).

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

3.2.14 *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-dimethylaminophenazothionium 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 one week.

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

3.2.16 *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.

3.3 Procedure

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.

Weigh accurately about 5 g of the sample, transfer to a 250 ml conical flask, add 50 ml of the hydrochloric acid (3.2.4) and fit a cold finger condenser (see Fig. 1, page 4) into the neck of the flask. Boil for 30 minutes and filter through a medium-textured, double acid-washed paper. Wash 6 times with the dilute hydrochloric acid (3.2.5) using a total quantity of about 20 ml. Discard the residual coal.

Add one drop of the hydrogen peroxide (3.2.6) to the filtrate and evaporate to dryness. Moisten the residue with the hydrochloric acid (3.2.3), 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 (3.2.12) and boil the solution. While still hot, add 2 or 3 drops of the mixed indicator solution (3.2.14) or the phenol red indicator solution (3.2.15), then add the sodium hydroxide solution (3.2.7) dropwise until the solution is just alkaline.

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To the hot solution add 10 ml of the barium chromate solution (3.2.8) dropwise from a pipette, stirring during the addition, and boil for 2 to 3 minutes, then add 10 ml of the sodium acetate solution (3.2.9). Boil for a further 2 to 3 minutes, then carefully add the ammonia solution (3.2.11) until the solution is distinctly alkaline; continue boiling until the excess ammonia is expelled, then allow to cool for 20 minutes.

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

(1) By gravity through an ashless, close-textured, double acid-washed filter paper of 10 to 12.5 cm 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 (3.2.10).

Add 1 to 2 g of the potassium iodide (3.2.2) to the filtrate, dissolve by swirling the vessel, then add 5 ml of the hydrochloric acid (3.2.3). Allow to stand for 5 minutes and titrate the liberated iodine with the sodium thiosulphate solution (3.2.13), using the starch indicator solution (3.2.16).

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.

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

3.4 Calculation of results

If W = weight of sample taken, expressed in grammes,

a = volume of sodium thiosulphate required in the full determination, expressed in millilitres,

b = volume of sodium thiosulphate required in the blank determination, expressed in millilitres,

F = normality of the sodium thiosulphate solution (i.e. 0.100 0, if the solution is exactly decinormal),

S_s = percentage of sulphate sulphur in the sample,

then

$$S_s = \frac{1.069\ F\ (a - b)}{W}$$

3.5 Tolerances

The results of duplicate determinations carried out at different times, in the same laboratory, on the same sample, by the same operator using the same apparatus, should not differ by more than 0.02 per cent of sulphate sulphur.

The means of the results of duplicate determinations carried out in different laboratories on representative samples taken from the same bulk after the last stage of reduction should not differ by more than 0.03 per cent of sulphate sulphur.

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4. PYRITIC SULPHUR — OXIDATION METHOD

4.1 Apparatus

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

4.2 Reagents

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

4.2.1 *Nitric acid.* Dilute 125 ml of nitric acid (specific gravity *d* 1.42) to 1 litre with water.

4.2.2 *Hydrogen peroxide*, 30 per cent (weight/volume) ("100 volumes").

4.2.3 *Hydrochloric acid.* Dilute 420 ml of hydrochloric acid (specific gravity *d* 1.18) to 1 litre with water.

4.2.4 *Sulphuric-phosphoric acid mixture.* Carefully mix 150 ml of sulphuric acid (specific gravity *d* 1.84) and 150 ml of phosphoric acid (specific gravity *d* 1.75). Add this to 600 ml of water, cool and dilute to 1 litre.

4.2.5 *Stannous chloride solution*, 10 per cent (weight/volume). Dissolve 5 g of anhydrous stannous chloride or 6 g of the dihydrate in 50 ml of hydrochloric acid (specific gravity *d* 1.18) and add this solution to 50 ml of water. Prepare this solution freshly before use.

4.2.6 *Mercuric chloride solution*, 6 per cent (weight/volume). Add 6 g of mercuric chloride to 100 ml of water and shake the mixture for 10 minutes.

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

4.2.8 *Potassium dichromate solution*, 0.017 9 N. Dissolve 0.878 0 g of potassium dichromate in water and dilute to 1 000 ml.

4.2.9 *Sodium diphenylamine sulphonate indicator solution*, 0.2 per cent. Dissolve 0.2 g of sodium diphenylamine sulphonate in water and dilute to 100 ml. Store in a dark bottle.

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4.3 Procedure

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 1 minute, preferably by mechanical means.

Weigh accurately about 1 g of the sample, transfer to a conical flask, add 50 ml of the nitric acid (4.2.1) and fit a cold finger condenser (see Fig. 1, page 4) into the neck of the flask. Boil for 30 minutes and filter through a medium-textured, double acid-washed paper. Wash 6 times with the nitric acid (4.2.1).

Add 2 ml of the hydrogen peroxide (4.2.2) to the filtrate and boil for 5 minutes to destroy any coloration arising from the decomposition of the coal.

Precipitate the iron by adding the ammonia solution (4.2.7) 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 (4.2.3) 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 should not exceed 20 ml by any considerable amount; if necessary, reduce the volume by evaporation before proceeding.

Heat to boiling and add the stannous chloride solution (4.2.5) dropwise, 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 mercuric chloride solution (4.2.6); a silky precipitate of mercurous chloride is formed.

Add 15 ml of the sulphuric-phosphoric acid mixture (4.2.4), dilute to between 150 and 200 ml with water, add 5 drops of the indicator solution (4.2.9) and titrate with the potassium dichromate solution (4.2.8). 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 dropwise 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 the "Determination of Sulphate Sulphur—Gravimetric Method" (see clause 2.3).

4.4 Calculation of results

If a = volume, expressed in millilitres, of potassium dichromate solution equivalent to the total iron in a sample weight of W, expressed in grammes,

b = volume, expressed in millilitres, of potassium dichromate solution equivalent to the non-pyritic iron in a sample weight of X, expressed in grammes, and

S_p = percentage of pyritic sulphur in the sample,

then

$$S_p = 0.115 \left(\frac{a}{W} - \frac{b}{X} \right)$$

4.5 Tolerances

The results of duplicate determinations carried out at different times, in the same laboratory, on the same sample, by the same operator using the same apparatus, should not differ

by more than 0.05 per cent for coals containing less than 0.5 per cent of pyritic sulphur;

nor

by more than 0.07 per cent for coals containing more than 0.5 per cent.

The means of the results of duplicate determinations carried out in different laboratories on representative samples taken from the same bulk after the last stage of reduction should not differ

by more than 0.10 per cent for coals containing less than 0.5 per cent of pyritic sulphur;

nor

by more than 0.15 per cent for coals containing more than 0.5 per cent.

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5. PYRITIC SULPHUR — REDUCTION METHOD

5.1 Apparatus

All graduated apparatus should be of the best analytical quality obtainable, and the balance used should be sensitive to 0.1 mg. The apparatus consists of the following (see Fig. 2 below):

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

5.1.2 *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.

5.1.3 *Mercury safety trap.*

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

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

5.1.6 *Cylinder*, containing compressed carbon dioxide.

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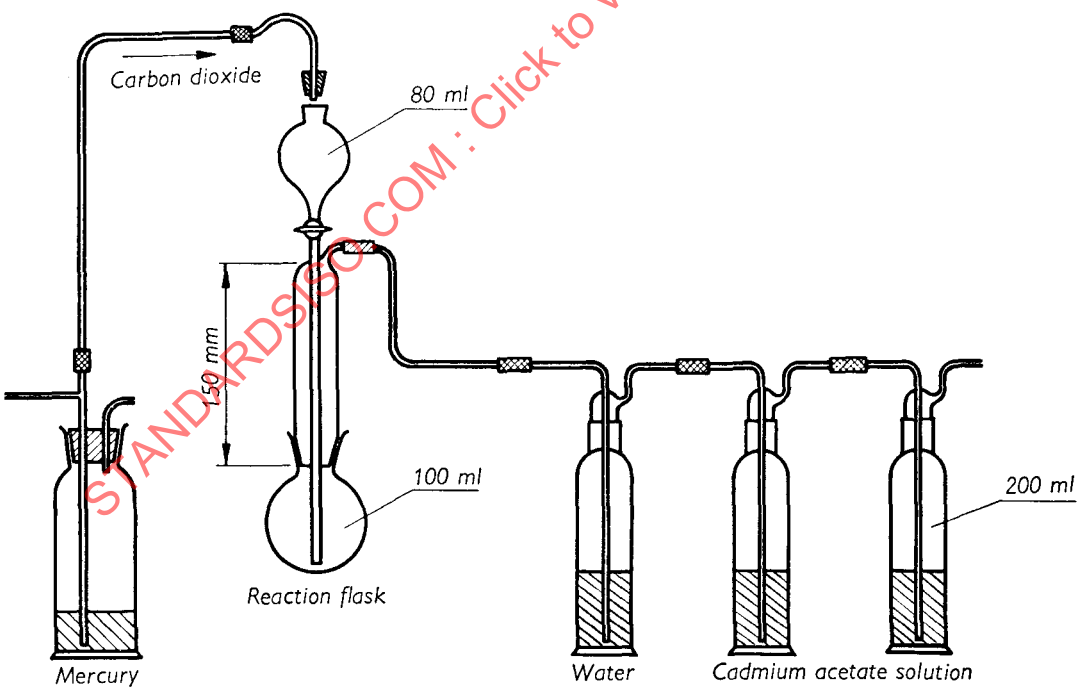

FIG. 2. — **Apparatus for determining pyritic sulphur**

5.2 Reagents

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

5.2.1 *Sodium carbonate*, anhydrous.

5.2.2 *Chromium metal*, powdered.

5.2.3 *Zinc metal*, granulated.

5.2.4 *Ethanol*, 95 per cent (weight/volume).

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

5.2.6 *Hydrochloric acid.* Dilute 525 ml of the hydrochloric acid (5.2.5) to 1 litre with water.

5.2.7 *Acetic acid*, glacial, specific gravity *d* 1.05.

5.2.8 *Cadmium acetate solution*, 4.3 per cent (weight/volume). Dissolve 50 g of cadmium acetate dihydrate in water, add 10 ml of glacial acetic acid (5.2.7) and dilute to 1 litre with water.

5.2.9 *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 the potassium iodide-iodate solution (5.2.11).

5.2.10 *Iodine solution*, approximately 0.1 N. 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 (5.2.9).

5.2.11 *Potassium iodide-iodate solution*, 0.031 25 N 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.

5.2.12 *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.

5.3 Procedure

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 1 minute, preferably by mechanical means. Grind 5 to 10 g of this sample until the particle size is such that at least 95 per cent is smaller than 0.02 mm (see Note 1, page 14). 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 (5.2.4), 15 g of the zinc (5.2.3) and 0.1 g of the chromium (5.2.2) 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 (5.2.5), to which 3 ml of the ethanol (5.2.4) 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 minutes. When the evolution of hydrogen ceases, after a further 15 to 20 minutes, pass a current of carbon dioxide to purge all hydrogen sulphide from the apparatus into the cadmium acetate absorbers (see Note 2, page 14).

Add to the absorber containing the precipitate of cadmium sulphide (see Note 3, page 14) a measured volume in sufficient excess of either the iodine solution (5.2.10) or the potassium iodide-iodate solution (5.2.11), add 20 ml of the hydrochloric acid (5.2.6) 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 (5.2.12) and titrate the excess iodine with the sodium thiosulphate solution (5.2.9).

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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 (5.2.4) for 30 minutes 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 (5.2.4) for 30 minutes 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 revolutions/minute (see Fig. 3, page 15).

   In either case, transfer the contents of the apparatus to a porcelain dish, dry for 30 minutes 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.

5.4 Calculation of results

If W = weight of sample, expressed in grammes,

a = volume of iodine or iodide-iodate solution taken, expressed in millilitres,

b = volume of sodium thiosulphate solution used, expressed in millilitres,

F_1 = normality of the iodine or iodide-iodate solution (i.e. 0.100 0 if the solution is exactly decinormal),

F_2 = normality of the sodium thiosulphate solution, and

S_p = percentage of pyritic sulphur in the sample,

then

$$S_p = \frac{1.6\ (a F_1 - b F_2)}{W}$$

5.5 Tolerances

The results of duplicate determinations carried out at different times in the same laboratory, on the same sample, by the same operator using the same apparatus, should not differ

by more than 0.05 per cent for coals containing less than 0.5 per cent of pyritic sulphur;

nor

by more than 0.07 per cent for coals containing more than 0.5 per cent.

The means of the results of duplicate determinations carried out in different laboratories on representative samples taken from the same bulk after the last stage of reduction should not differ

by more than 0.10 per cent for coals containing less than 0.5 per cent of pyritic sulphur;

nor

by more than 0.15 per cent for coals containing more than 0.5 per cent.

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