INTERNATIONAL STANDARD

ISO 157

Second edition
1996-06-01

Coal — Determination of forms of sulfur

Charbon — Détermination de la teneur en différentes formes de soufre

Reference number
ISO 157:1996(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 157 was prepared by Technical Committee ISO/TC 27, *Solid mineral fuels*, Subcommittee SC 5, *Methods of analysis*.

This second edition cancels and replaces the first edition (ISO 157:1975), of which it constitutes a technical revision.

Annex A of this International Standard is for information only.

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland

Printed in Switzerland

Introduction

For many purposes, a knowledge of the total sulfur content of a coal is sufficient, but for certain work it is also necessary to know how the sulfur is distributed between the coal substance and the mineral matter. In particular, such information may be required in connection with coal classification and cleaning.

Sulfur is usually present in coal in three forms, viz:

a) sulfate sulfur, i.e. the sulfur present in the form of inorganic sulfates;

b) pyritic sulfur, i.e. the sulfur present in the form of pyrites and marcasite;

c) organic sulfur, i.e. the sulfur present in the form of organic sulfur compounds.

This page intentionally left blank

Coal — Determination of forms of sulfur

Section 1: General

1.1 Scope

This International Standard specifies methods of determining the sulfate and pyritic sulfur contents of coals, including brown coals and lignites, and of calculating the amount of organic sulfur present.

1.2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 331:1983, *Coal — Determination of moisture in the analysis sample — Direct gravimetric method.*

ISO 334:1993, *Solid mineral fuels — Determination of total sulfur — Eschka method.*

ISO 351:1995, *Solid mineral fuels — Determination of total sulfur — High temperature combustion method.*

ISO 1015:1992, *Brown coals and lignites — Determination of moisture content — Direct volumetric method.*

ISO 1170:1977, *Coal and coke — Calculation of analyses to different bases.*

ISO 1988:1975, *Hard coal — Sampling.*

ISO 5068:1983, *Brown coals and lignites — Determination of moisture content — Indirect gravimetric method.*

ISO 5069-2:1983, *Brown coals and lignites — Principles of sampling — Part 2: Sample preparation for determination of moisture content and for general analysis.*

1.3 Principle

The procedure described in this International Standard utilizes the differential solubilities of sulfates and pyrites in dilute hydrochloric and nitric acids under reflux conditions, such that each can be taken in solution successively and determined directly.

A general schematic representation of the procedure is given in figure 1.

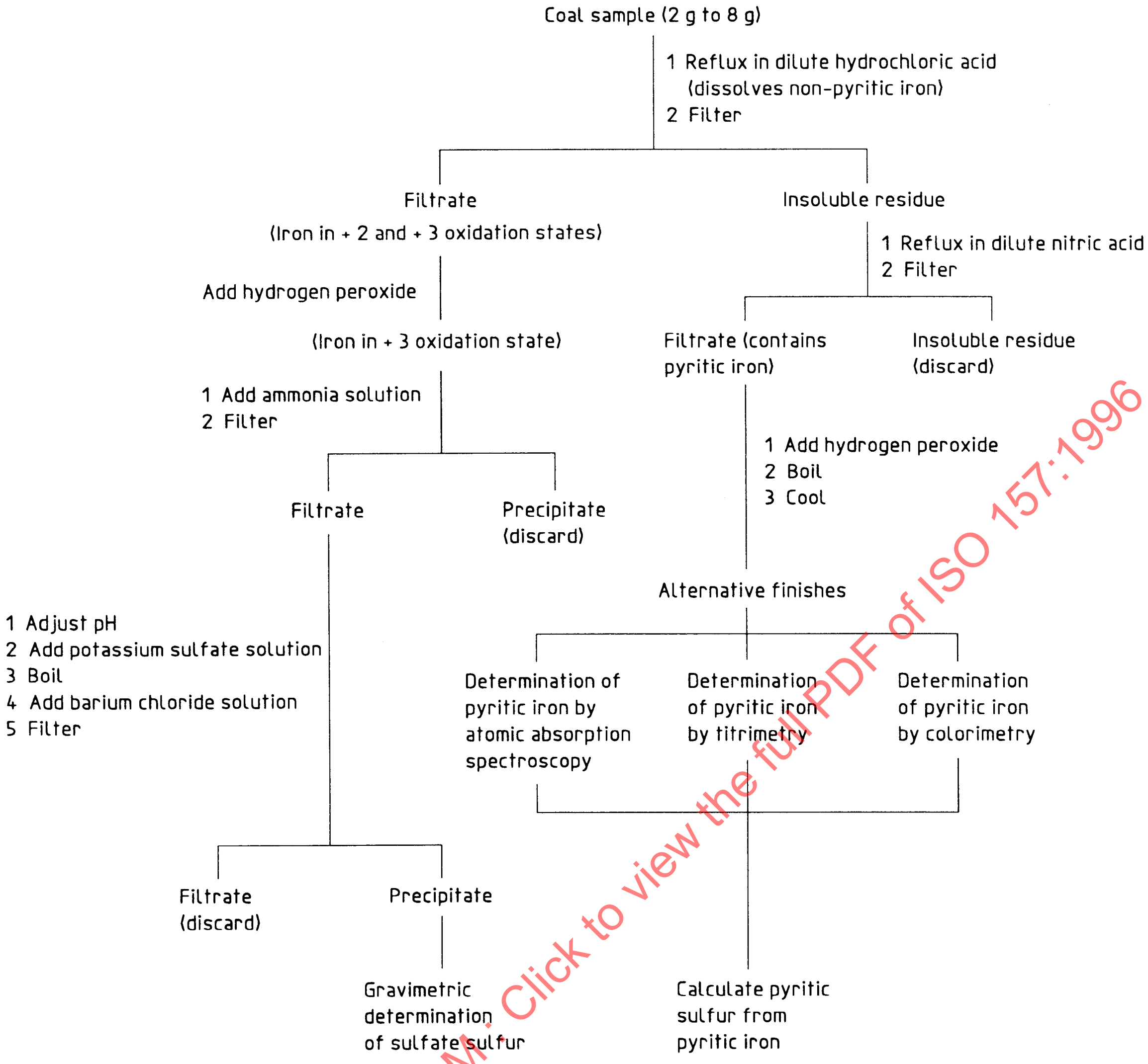
1.4 Preparation of the test sample

The test sample is the general analysis test sample prepared in accordance with ISO 1988 or ISO 5069-2, as appropriate.

Grind about 25 g of the sample to pass a sieve of aperture 75 µm and ensure that its moisture content is in equilibrium with the laboratory atmosphere, exposing it if necessary in a thin layer for the minimum time required to achieve equilibrium.

Before commencing the determination, thoroughly mix the test sample for at least 1 min, preferably by mechanical means.

If the results are to be calculated other than on an air-dried basis (see 6.1) then, after weighing the test portion (see 2.4), determine the moisture content using a further portion of the test sample by the method described in ISO 331, ISO 1015 or ISO 5068, as appropriate.



NOTE — Organic sulfur = Total sulfur − (sulfate sulfur + pyritic sulfur)

Figure 1 — General schematic representation of the procedure

Section 2: Separation of sulfate and pyritic sulfur

2.1 Principle

The test portion is extracted with dilute hydrochloric acid to bring both the sulfate sulfur and the non-pyritic iron into solution. The pyritic iron and sulfur remain in the residue which is separated by filtration.

2.2 Reagents

WARNING — Care must be exercised when handling the reagents, many of which are toxic and corrosive.

During the analysis, unless otherwise stated, use only reagents of recognized analytical reagent grade and only distilled water or water of equivalent quality.

2.2.1 Hydrochloric acid, concentrated, approximately 36 % (*m*/*m*).

2.2.2 Hydrochloric acid, dilute, approximately 15 % (*m*/*m*).

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

2.2.3 Nitric acid, dilute, approximately 9 % (*m*/*m*).

Dilute 130 ml of concentrated nitric acid [approximately 70 % (*m*/*m*)] to 1 litre with water.

2.3 Apparatus

2.3.1 Analytical balance, capable of weighing to the nearest 0,1 mg.

2.3.2 Graduated glassware, conforming to the requirements for class A in the International Standards prepared by ISO/TC 48, *Laboratory glassware and related apparatus.*

2.3.3 Cold-finger condenser, to fit loosely into the neck of a 250 ml conical flask (see figure 2).

Approximate dimensions in millimetres

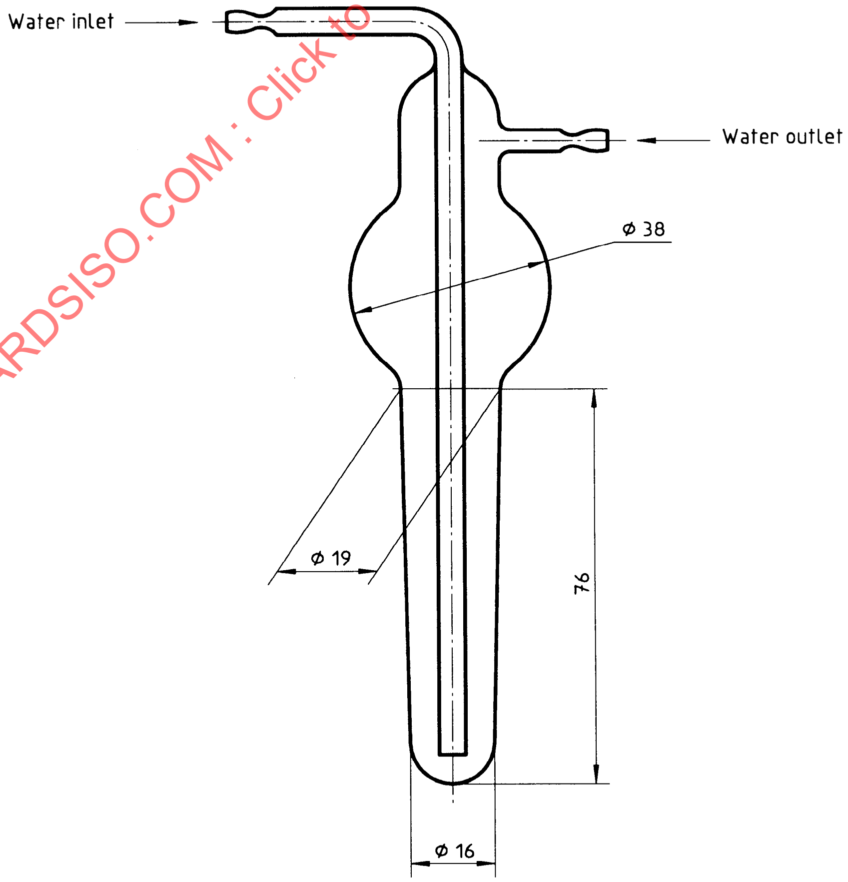


Figure 2 — Cold-finger condenser for the determination of sulfate and pyritic sulfur

2.4 Procedure

2.4.1 Test portion

Take a test portion of the mass given in table 1 for the expected total sulfur content, weighing to the nearest 0,1 mg.

Table 1 — Test portion

Total sulfur content % (*m*/*m*)	Mass of test portion g
< 0,7	8
0,7 to 2,0	5
> 2,0	2

2.4.2 Extraction

Transfer the test portion to a 250 ml conical flask, add 50 ml of the dilute hydrochloric acid (2.2.2) and fit the cold-finger condenser (2.3.3) into the neck of the flask. Boil for 30 min, ensuring that a slow stream of water is passing through the cold finger. Remove the condenser and thoroughly rinse back into the flask. Filter the mixture through a medium-textured, doubly acid-washed filter paper into a tall-form beaker. Wash the residue three times with the dilute hydrochloric acid (2.2.2) and a further three times with hot distilled water, using a total volume of approximately 30 ml. Retain the filtrate for the determination of sulfate sulfur (see Section 3). Immediately transfer the washed, undissolved residue and filter paper to a 250 ml conical flask, add 50 ml of the dilute nitric acid (2.2.3) and retain for the determination of pyritic sulfur (see Section 4).

Section 3: Determination of sulfate sulfur

3.1 Principle

The sulfate sulfur extracted by dilute hydrochloric acid from the test portion is determined gravimetrically by precipitation with barium chloride.

3.2 Reagents

WARNING — Care must be exercised when handling the reagents, many of which are toxic and corrosive.

During the analysis, unless otherwise stated, use only reagents of recognized analytical reagent grade and only distilled water or water of equivalent purity.

3.2.1 Hydrogen peroxide, solution, approximately 30 % (*m*/*m*).

3.2.2 Methyl red, indicator solution.

Dissolve 1 g of 2-(4-dimethylaminophenylazo)benzoic acid, sodium salt (methyl red) in 1 litre of water.

3.2.3 Ammonia, concentrated, solution not less than 25 % (*m*/*m*).

3.2.4 Hydrochloric acid, concentrated, approximately 36 % (*m*/*m*).

3.2.5 Potassium sulfate, approximately 2 g/l solution.

Dissolve approximately 2 g of potassium sulfate in water and dilute to 1 litre.

3.2.6 Barium chloride, approximately 85 g/l solution.

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

3.2.7 Silver nitrate, approximately 17 g/l solution.

Dissolve 17 g of silver nitrate in water and dilute to 1 litre. Store in a dark glass bottle.

3.3 Apparatus

3.3.1 Analytical balance, capable of weighing to the nearest 0,1 mg.

3.3.2 Graduated glassware, conforming to the requirements for class A in the International Standards prepared by ISO/TC 48.

3.3.3 Electrically-heated muffle furnace, capable of being maintained at 800 °C ± 25 °C, with an adequate ventilation rate.

3.3.4 Crucible, of platinum, silica or glazed porcelain, of capacity approximately 25 ml.

3.3.5 Flat plate, 6 mm thick, of silica or other suitable refractory material, which fits easily into the muffle furnace (3.3.3).

3.3.6 Gooch crucible, of glazed porcelain or sintered glass.

3.3.7 Air oven, capable of being maintained at a temperature of 130 °C ± 10 °C.

3.3.8 Filter cone, made of porcelain, of diameter 25 mm.

3.4 Procedure

To the filtrate from the hydrochloric acid extraction (see 2.4.2), add 5 ml of the hydrogen peroxide solution (3.2.1) and boil for 5 min to convert all the soluble iron to the + 3 oxidation state. While still hot, add 2 or 3 drops of the methyl red indicator solution (3.2.2) followed by the ammonia solution (3.2.3), drop by drop, until the solution is just alkaline (yellow colour) and then add a further 5 drops in excess. Filter the resultant precipitate on a toughened fast filter paper into a 250 ml beaker. Wash thoroughly with hot water, discarding the precipitate. Cautiously add the concentrated hydrochloric acid (3.2.4) to the filtrate, drop by drop, until the colour of the solution changes to pink and then add a further 1 ml in excess. The volume of the solution shall be between 150 ml and 250 ml.

Add 25,0 ml of the potassium sulfate solution (3.2.5) from a one-mark pipette. Cover the beaker with a watch glass, 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 (3.2.6) from a pipette with a delivery time of approximately 20 s, held so that the barium chloride falls into the centre of the hot solution, whilst this is being agitated. Keep the solution just below boiling point, without agitation, for 30 min.

Filter the solution using one of the following techniques.

a) By gravity through an ashless, close-textured, doubly acid-washed filter paper of diameter 100 mm to 125 mm. Carefully fold the filter paper and fit it into a fluted, long-stemmed 60° funnel, so that the stem remains full of liquid during the filtration.

b) By gravity through a filter-paper pad prepared from ashless, doubly acid-washed filter paper. To prepare the filter-paper pad, shake doubly acid-washed filter-paper clippings, in pieces of area approximately 1 cm^2, with water in a bottle until the paper is thoroughly disintegrated. Place a filter cone (3.6.8) in a filter funnel of diameter 75 mm, close the stem of the funnel with a finger and add water until the cone is immersed and the funnel stem is full. Shake sufficient paper pulp onto the cone 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. After transferring the filter-paper pad to the crucible, wipe the funnel successively with two halves of an ashless filter paper which are then incinerated with the pad.

c) By suction through a pad of mineral fibre used for filtration in a Gooch crucible. Before commencing the filtration, dry the Gooch crucible and pad for 1 h at a temperature of 130 °C ± 10 °C and weigh them.

Wash the precipitate 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 the silver nitrate solution (3.2.7).

If technique a) or b) is used, place the wet filter paper or pad in the previously ignited and weighed crucible (3.3.4) on the cold, flat plate (3.3.5) and insert it into the muffle furnace (3.3.3) for 15 min at a temperature of 800 °C ± 25 °C. Cool in a desiccator and reweigh.

If technique c) is used, dry the Gooch crucible and pad for 1 h at a temperature of 130 °C ± 10 °C, cool in a desiccator and reweigh.

3.5 Blank test

Carry out a blank test using the same procedure as described in 2.4.2 and 3.4, but omitting the test portion. Using a pipette, add 25,0 ml of the potassium sulfate solution (3.2.5) to the filtrate before adding the methyl red indicator solution (3.2.2).

3.6 Expression of results

The sulfate sulfur content, $w_{\mathrm{S,s}}$, of the sample, expressed as a percentage by mass, is given by the equation

$$w_{\mathrm{S,s}} = \frac{m_2 - m_3}{m_1} \times 13{,}74$$

where

m_1 is the mass, in grams, of the test portion taken for hydrochloric acid extraction;

m_2 is the mass, in grams, of barium sulfate found in the determination;

m_3 is the mass, in grams, of barium sulfate found in the blank test.

NOTE 1 The derivation of the factor used in this calculation is given in A.1 in annex A.

Report the result, as the mean of duplicate determinations, to the nearest 0,01 % (*m*/*m*).

3.7 Precision

3.7.1 Repeatability limit

The results of duplicate determinations, carried out at different times, in the same laboratory, by the same operator with the same apparatus on representative portions taken from the same test sample, should not differ by more than 0,02 % absolute.

3.7.2 Reproducibility critical difference

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, should not differ by more than 0,03 % absolute, at a 95 % confidence level.

Section 4: Determination of pyritic sulfur

NOTE 2 This method may be used to determine the pyritic sulfur content of all types of coal. However, the titrimetric finish may be unsatisfactory for brown coals and lignites and it is therefore recommended that, in such cases, only the colorimetric or atomic absorption spectrometric finish be used.

4.1 Principle

The insoluble residue from the hydrochloric acid digestion (see 2.4.2) is further extracted with dilute nitric acid to bring the pyritic iron into solution. The amount of iron present is then determined by either titrimetric, colorimetric or atomic absorption spectrometric techniques. The pyritic sulfur content of the original test sample is calculated from this pyritic iron concentration, assuming the 1:2 stoichiometry of FeS_2.

4.2 Reagents

WARNING — Care must be exercised when handling the reagents, many of which are toxic and corrosive.

During the analysis, unless otherwise stated, use only reagents of recognized analytical reagent grade and only distilled water or water of equivalent purity.

4.2.1 Titrimetric, colorimetric and atomic absorption spectrometric finishes

4.2.1.1 Nitric acid, dilute approximately 9 % (*m/m*).

Dilute 130 ml of concentrated nitric acid [approximately 70 % (*m/m*)] to 1 litre with water.

4.2.1.2 Hydrogen peroxide, solution, approximately 30 % (*m/m*).

4.2.2 Titrimetric finish only

4.2.2.1 Ammonia, concentrated solution, not less than 25 % (*m/m*).

4.2.2.2 Hydrochloric acid, dilute, approximately 15 % (*m/m*).

Dilute 420 ml of concentrated hydrochloric acid (2.2.1) to 1 litre with water.

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

Dissolve 5 g anhydrous tin(II) chloride, or 6 g of the dihydrate, in 50 ml of concentrated hydrochloric acid (2.2.1) warming as necessary. Add this solution to 40 ml of water, cool and dilute to 100 ml.

Prepare this solution freshly before use.

4.2.2.4 Mercury(II) chloride, saturated solution.

Add 7 g mercury(II) chloride to 100 ml of water and shake the mixture for 10 min.

4.2.2.5 Sulfuric/orthophosphoric acid mixture.

Cautiously add 150 ml of sulfuric acid [approximately 98 % (*m/m*)] to approximately 500 ml of water. After allowing the mixture to cool, add 150 ml of orthophosphoric acid solution [approximately 85 % (*m/m*)] and dilute to 1 litre with water.

4.2.2.6 Sodium diphenylamine sulfonate indicator, 2 g/l solution.

Dissolve 0,2 g of sodium diphenylamine sulfonate in water and dilute to 100 ml.

Store in a dark glass bottle.

4.2.2.7 Potassium dichromate, standard volumetric solution, $c(K_2Cr_2O_7) = 0{,}003$ mol/l.

Dissolve 0,882 6 g of potassium dichromate (previously dried for 2 h at 150°C) in water and dilute to 1 litre in a volumetric flask.

4.2.2.8 Methyl red, indicator solution.

Dissolve 1 g of 2-(4-dimethylaminophenylazo)benzoic acid, sodium salt (methyl red) in 1 litre of water.

4.2.3 Colorimetric and atomic absorption spectrometric finishes

4.2.3.1 Iron, standard stock solution.

Dissolve 0,100 0 g of pure iron wire in 2,5 ml of concentrated nitric acid [approximately 70 % (*m/m*)] and 7,5 ml of water. Boil to expel oxides of nitrogen, cool and dilute with water to 100 ml in a volumetric flask. 1 ml of this stock solution contains 1 mg of Fe.

4.2.4 Colorimetric finish only

4.2.4.1 Hydroxylammonium chloride, 100 g/l solution.

Dissolve 10 g of hydroxylammonium chloride in water and dilute to 100 ml.

4.2.4.2 Congo red, indicator paper.

4.2.4.3 Sodium acetate, 328 g/l solution.

Dissolve 32,8 g of anhydrous sodium acetate in water and dilute to 100 ml.

4.2.4.4 Phenanthroline, indicator solution.

Dissolve 0,625 g of 1,10-phenanthroline hydrate or hydrochloride in water and dilute to 250 ml.

Store in a dark glass bottle and discard the solution if a brown colour develops.

4.2.5 Atomic absorption spectrometric finish only

4.2.5.1 Lanthanum(III) chloride, solution containing 100 g/l of lanthanum.

Dissolve 267 g of lanthanum(III) chloride heptahydrate in water and dilute to 1 litre.

4.3 Apparatus

4.3.1 Analytical balance, capable of weighing to the nearest 0,1 mg.

4.3.2 Graduated glassware, conforming to the requirements for Class A in the International Standards prepared by ISO/TC 48.

4.3.3 Cold-finger condenser, to fit loosely into the neck of a 250 ml conical flask (see figure 2).

4.3.4 UV/visible spectrometer, capable of measuring absorption at 510 nm.

4.3.5 Atomic absorption spectrometer, capable of measuring absorption at 248,3 nm and 372,0 nm.

4.4 Procedure

4.4.1 Preparation of test solution

Take the 250 ml conical flask, retained from the hydrochloric acid extraction (see 2.4.2) and macerate the residue and filter paper immersed in the nitric acid, with a flat-ended glass rod, rinsing the rod on withdrawal. Fit the cold-finger condenser (4.3.3) into the neck of the flask and boil the mixture for 30 min, ensuring that a slow stream of water is passing through the cold finger. Remove the condenser, rinse thoroughly into the conical flask and filter the mixture through a medium-textured, doubly acid-washed filter paper into a beaker. Wash the residue three times with dilute nitric acid solution (4.2.1.1) and a further three times with hot water, using a total volume of about 30 ml. Discard the undissolved residue.

Add 5 ml of the hydrogen peroxide solution (4.2.1.2) to the filtrate and boil for 5 min to destroy any coloration arising from the decomposition of the coal. Allow to cool and determine the iron content of this test solution by one on the methods outlined in 4.4.2, 4.4.3 or 4.4.4.

4.4.2 Titrimetric finish

Heat the test solution from 4.4.1 until it boils, add two or three drops of methyl red indicator solution (4.2.2.8) and precipitate the iron present by adding the ammonia solution (4.2.2.1), drop by drop, until a slight excess is present (yellow colour) and then add 5 drops in excess. Filter on a toughened, fast filter paper and wash the precipitate thoroughly with hot water. Pierce the filter paper and wash the precipitate into a 500 ml beaker with a fine jet of hot water. Pour 10 ml of hot dilute hydrochloric acid (4.2.2.2) onto the filter in small portions to remove the last traces of iron and finally wash with a small quantity of hot water. It is important that all the iron precipitate be removed by washing. If necessary, warm the solution to dissolve the iron hydroxide.

Heat the solution until it boils and reduce the volume to approximately 20 ml by evaporation. Add the tin(II) chloride solution (4.2.2.3), drop by drop, to the hot solution from a pipette or dropping bottle, stirring until the yellow colour disappears. Add 5 drops in excess, cool the solution quickly to room temperature and rapidly add 10 ml of the mercury(II) chloride solution (4.2.2.4). A silky precipitate of mercury(I) chloride is formed.

Add 15 ml of the sulfuric/orthophosphoric acid mixture (4.2.2.5), dilute the solution to between 150 ml and 200 ml with water, add 5 drops of the sodium diphenylamine sulfonate indicator solution (4.2.2.6) and titrate against the potassium dichromate standard volumetric solution (4.2.2.7). 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. At this stage, add the potassium dichromate drop by drop until the colour changes permanently to an intense violet-blue. Note the titration volume, in millilitres.

NOTE 3 Samples containing more than 2 % (*m*/*m*) of pyritic sulfur will require large volumes of potassium dichromate standard volumetric solution for titration. To avoid this, the solution to be titrated should be diluted with water to a standard volume in a volumetric flask and a suitable aliquot taken from this by pipette for the titration, with an appropriate adjustment being made in the calculation.

4.4.3 Colorimetric finish

4.4.3.1 Preparation of the set of calibration solutions

Using a one-mark pipette, transfer 20 ml of the iron standard stock solution (4.2.3.1) to a 500 ml volumetric flask, dilute to the mark with water and mix thoroughly. Transfer 1 ml, 2 ml, 3 ml ... 10 ml aliquots of this solution (taken using one-mark pipettes) into separate 50 ml volumetric flasks. Dilute each aliquot to 25 ml with water, add 5 ml of the hydroxylammonium chloride solution (4.2.4.1) and a small square of the Congo red indicator paper (4.2.4.2). Titrate the mixture with the sodium acetate solution (4.2.4.3) until the indicator turns red. Add 4 ml of the phenanthroline indicator solution (4.2.4.4) and dilute to 50 ml with water. Mix thoroughly and leave to stand for 1 h.

4.4.3.2 Determination

Dilute the prepared test solution (see 4.4.1) with water in a volumetric flask and make up to 250 ml. Mix thoroughly.

Pipette *a* ml (see table 2) from this flask into a 50 ml volumetric flask and add 20 ml of water, 5 ml of the hydroxylammonium chloride solution (4.2.4.1) and a small square of the Congo red indicator paper (4.2.4.2). Titrate the mixture with the sodium acetate solution (4.2.4.3) until the indicator paper turns red. Add 4 ml of the phenanthroline indicator solution (4.2.4.4) and dilute 50 ml with water. Mix thoroughly and leave to stand for 1 h.

Measure the absorbance of the calibration solution (4.4.3.1) and the solution prepared in this subclause with the UV/visible spectrometer (4.3.4), at a wavelength of 510 nm using a cell of suitable path length, against water (see note 4). Convert the absorbance value of the diluted test solution to mass of iron, in micrograms, by reference to the calibration curve (4.4.3.3).

NOTE 4 The calibration and determination should, preferably, be carried out using cells of the same size. If cells of different sizes are used, an appropriate adjustment should be made in the final calculation.

Table 2 — Aliquot *a* for colorimetric finish

Expected total sulfur content % (*m*/*m*)	Aliquot *a* ml
< 0,7	2
⩾ 0,7	1

4.4.3.3 Preparation of the calibration curve

Prepare a calibration curve by plotting the absorbance measured by the UV/visible spectrometer against the iron content, in micrograms, of the calibration solutions (4.4.3.1).

4.4.4 Atomic absorption spectrometric finish

4.4.4.1 Preparation of the set of calibration solutions

Prepare a set of calibration solutions to cover the expected range of concentration by transferring the appropriate volumes of the iron standard stock solution (4.2.3.1) to a series of 100 ml volumetric flasks. Add 20 ml of the dilute nitric acid (4.2.1.2) and 4 ml of the lanthanum(III) chloride solution (4.2.5.1) to each volumetric flask. Dilute to the mark with water and mix thoroughly.

4.4.4.2 Determination

To the prepared test solution (see 4.4.1), add 10 ml of the lanthanum(III) chloride solution (4.2.5.1). Dilute with water to 250 ml in a volumetric flask and mix thoroughly.

Adjust the atomic absorption spectrometer to the wavelength for iron. Fit the correct burner and, in accordance with the instructions of the instrument manufacturer, light the appropriate flame.

Suitable conditions for the determination of iron are given in table 3.

Table 3 — Suitable spectrometric conditions

	Linear range	
	0 to 100 mg Fe/l	0 to 9 mg Fe/l
Wavelength	372,0 nm	248,3 nm
Slit width	0,2 nm	0,2 nm
Burner length	50 mm	50 mm
Flame	Air/acetylene1)	Air/acetylene1)

1) Lean, as defined in the manufacturer's instructions.

Measure the absorbance of the calibration solution (4.4.4.1) and the solution prepared in this subclause with the atomic absorption spectrometer (4.3.5), and record the readings when stable responses are obtained for the absorbance values. Repeat the readings at least twice more and convert the net absorbance value to iron concentration, by reference to the calibration curve (4.4.4.3).

NOTES

5 Water should be used to zero the spectrometer and to rinse during calibration and testing.

6 If the iron concentration of the test solution is such that it exceeds the linear range, appropriate additional dilution of the original diluted test solution should be made. Care should be taken, however, to maintain the concentrations, of lanthanum chloride and nitric acid relative to the original test solution.

4.4.4.3 Preparation of the calibration curve

Prepare a calibration curve by plotting the absorbance measured by the atomic absorption spectrometer against the iron concentration, in micrograms per millilitre, of the calibration solutions (4.4.4.1).

4.5 Blank test

Prepare a blank test solution at the same time and using the same procedure as described in 2.4.2 and 4.4.1, but omitting the test portion. Note the titration volume, in millilitres.

Determine the iron concentration of the blank test solution using the same procedure as described in 4.4.2, 4.4.3 or 4.4.4 at the same time.

4.6 Expression of results

4.6.1 Titrimetric finish

Using the titrimetric finish (see 4.4.2), the pyritic sulfur content, $w_{S,p}$, expressed as a percentage by mass of the sample, is given by the equation

$$w_{S,p} = \frac{V_1 - V_2}{m_1} \times 0{,}115\,4$$

where

V_1 is the volume, in millilitres, of potassium dichromate solution equivalent to the pyritic iron in the test solution (see 4.4.2);

V_2 is the volume, in millilitres, of potassium dichromate solution equivalent to the pyritic iron in the blank test solution (see 4.5);

m_1 is the mass, in grams, of the original test portion taken for hydrochloric acid extraction (see 2.4.1).

NOTE 7 The derivation of the factor used in this calculation is given in A.2 in annex A.

Report the result, as the mean of duplicate determinations, to the nearest 0,01 %.

4.6.2 Colorimetric finish

Using the colorimetric finish (see 4.4.3), the pyritic sulfur content, $w_{S,p}$, of the sample, expressed as a percentage by mass, is given by the equation

$$w_{S,p} = \frac{m_4 - m_5}{V_3 \times m_1} \times 0{,}028\,7$$

where

m_4 is the mass, in micrograms, of iron in the diluted test solution (see 4.4.3.2);

m_5 is the mass, in micrograms, of iron in the blank test solution (see 4.5);

m_1 is the mass, in grams, of the original test portion taken for hydrochloric acid extraction (see 2.4.1);

V_3 is the volume, in millilitres, of the aliquot taken from the diluted test solution (see 4.4.3.2).

NOTE 8 The derivation of the factor used in this calculation is given in A.3 in annex A.

Report the result, as the mean of duplicate determinations, to the nearest 0,01 %.

4.6.3 Atomic absorption spectrometric finish

Using the atomic absorption spectrometric finish (see 4.4.4), the pyritic sulfur content, $w_{S,p}$, of the sample, expressed as a percentage by mass, is given by the equation

$$w_{S,p} = \frac{\rho_{Fe,1} - \rho_{Fe,2}}{m_1} \times 0{,}028\,7$$

where

$\rho_{Fe,1}$ is the concentration of iron, in micrograms per millilitre, in the diluted test solution (see 4.4.4.2);

$\rho_{Fe,2}$ is the concentration of iron, in micrograms per millilitre, in the blank test solution (see 4.5);

m_1 is the mass, in grams, of the original test portion taken for hydrochloric acid extraction (see 2.4.1).

NOTE 9 The derivation of the factor used in this calculation is given in A.4 in annex A.

Report the result, as the mean of duplicate determinations, to the nearest 0,01 %.

4.7 Precision

4.7.1 Repeatability limit

The results of duplicate determinations, carried out at different times, in the same laboratory, by the same operator, with the same apparatus, on representative portions taken from the same test sample, should not differ by more than the value shown in table 4.

4.7.2 Reproducibility critical difference

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, should not differ by more than the value shown in table 4, at the 95 % confidence limit.

Table 4 — Precision

Pyritic sulfur content %	**Maximum acceptable difference between results** (calculated to the same moisture content)	
	Repeatability limit	**Reproducibility critical difference**
< 0,5	0,05 % absolute	0,10 % absolute
0,5 to 1,5	0,07 % absolute	0,15 % absolute
> 1,5	5 % of the result	10 % of the result

Section 5: Determination of organic sulfur

5.1 Principle

Under the conditions described in this International Standard, organic sulfur is insoluble in both dilute hydrochloric acid and dilute nitric acid and is thus determined, by difference, from the total sulfur content and the sulfate and pyritic sulfur contents.

5.2 Calculation

Calculate the percentage of organic sulfur in the sample, by subtracting the sum of the percentages of sulfate and pyritic sulfur from the percentage of total sulfur in the sample, as determined by the method given in ISO 334 or ISO 351.

Report the result, as the mean of duplicate determinations, to the nearest 0,01 %.