International Standard 4934

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Steel and cast iron — Determination of sulphur content — Gravimetric method

Aciers et fontes — Dosage du soufre — Méthode gravimétrique

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Foreword

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It has been approved by the member bodies of the following countries :

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Steel and cast iron — Determination of sulphur content — Gravimetric method

1 Scope and field of application

This International Standard specifies a gravimetric method for the determination of the sulphur content of steels and cast iron, excluding steels containing selenium. The method is particularly suitable as a reference method for the standardization of samples on which certified standard values are to be established.

The method is applicable to products having sulphur contents greater than 0,003 % (*m/m*).

2 References

ISO/R 377, *Selection and preparation of samples and test pieces for wrought steel.* [1)]

ISO 565, *Test sieves — Woven metal wire cloth and perforated plate — Nominal sizes of apertures.*

3 Principle

Dissolution of a test portion in dilute nitric acid in the presence of bromine, or in dilute nitric acid and concentrated hydrochloric acid in the presence of bromine (with the aid of an appropriate device to prevent sulphur losses). Addition of hydrofluoric acid and perchloric acid and evaporation of the solution until white fumes of perchloric acid are evolved. If necessary, volatilization of chromium as chromyl chloride. Chromatographic separation of the sulphate ions in an alumina column and elution with ammonium hydroxide solution. Precipitation of the sulphate ions as barium sulphate under carefully controlled conditions and filtering, washing, heating and weighing.

4 Reagents

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

4.1 Aluminium oxide (alumina), prepared for chromatography, of particle size corresponding to a sieve mesh size of 75 to 150 µm (supplementary series R 40/3 of ISO 565). Alumina designated alkaline, neutral or acid may be used.

Place about 200 g of the dry alumina in a 400 ml beaker containing 300 ml of water and place the beaker in a sink. Insert a glass tube having a bore of 5 mm such that it extends to the bottom of the beaker and connect the tube to a water supply. Adjust the water flow so that the suspended fine material overflows the rim of the beaker. Continue this treatment until all the fine material, which does not settle within 1 min of stopping the water flow, is removed.

Pour off the supernatant liquid from the coarser material, add the hydrochloric acid (4.4) in an amount sufficient to cover the alumina, stir and allow to stand for not less than 12 h.

Pour off the hydrochloric acid and wash the alumina with water as described in the second paragraph.

For preparation of the column, make a slurry of the washed alumina and the hydrochloric acid solution (4.8).

4.2 Bromine.

4.3 Nitric acid, ϱ approximately 1,40 g/ml.

4.4 Nitric acid, 1 + 1 dilution.

4.5 Hydrochloric acid, ϱ approximately 1,19 g/ml.

4.6 Hydrochloric acid, 1 + 1 dilution.

4.7 Hydrochloric acid, 1 + 9 dilution.

4.8 Hydrochloric acid, 1 + 19 dilution.

4.9 Perchloric acid, ϱ approximately 1,54 g/ml.

NOTE — If this reagent is shown to have a high sulphate content, this may be removed by passing the reagent through the adsorption column (5.3).

4.10 Perchloric acid, 1 + 98 dilution.

4.11 Hydrofluoric acid, ϱ approximately 1,14 g/ml.

4.12 Ammonium hydroxide, ϱ approximately 0,90 g/ml.

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4.13 Ammonium hydroxide, 1 + 19 dilution.

4.14 Ammonium hydroxide, 1 + 99 dilution.

4.15 Iron(II) perchlorate solution.

Transfer 5 g of high purity iron of very low sulphur content to a 500 ml narrow-necked conical flask, and dissolve in a mixture of 25 ml of the perchloric acid (4.9) and 375 ml of water by heating in a water bath at 50 °C.

When about two-thirds of the iron has dissolved, remove the flask from the water bath and allow it to cool.

Close the flask with a rubber stopper provided with a one-way valve to permit the escape of gases without the ingress of air.

4.16 Sulphuric acid, solution corresponding to approximately 48 mg of sulphur per litre.

Add 2,8 ml of sulphuric acid, ϱ approximately 1,84 g/ml, to about 500 ml of water. Dilute to 1 000 ml and mix. Take 30 ml of this solution, dilute to 1 000 ml and mix.

4.17 Barium chloride dihydrate, 1,22 g/l solution.

Dissolve 1,22 g of barium chloride dihydrate ($BaCl_2.2H_2O$) in water, dilute to 1 000 ml and mix.

Filter this solution through a non-hardened, close texture filter paper just before use.

1 ml of this solution is equivalent to approximately 0,16 mg of sulphur.

4.18 Methyl orange, 0,50 g/l solution.

5 Apparatus

Normal laboratory apparatus, and

5.1 Conical flask, of capacity 1 000 ml, having a ground-glass neck.

5.2 Allihn condenser (four or six bulb type).

5.3 Adsorption column (see the figure).

Prepare the adsorption column as follows.

Fit the column tube into a one-hole rubber bung just below the reservoir to act as a gasket for fixing the tube in a suction filtration flask. Fit the tube into the suction flask and place a well-packed plug of quartz wool, about 20 mm thick, in the narrow end of the tube. Transfer sufficient alumina slurry (4.1) into the tube to make a column 100 to 120 mm long. Using the hydrochloric acid solution (4.8), rinse all the alumina particles from the sides of the reservoir into the tube. Insert a plug of quartz wool and press down with a glass rod so that the quartz wool makes contact with the alumina. Compact the plug again if contact is not maintained with the alumina column. Ensure that all alumina particles are removed from the column sides above the top plug.

Add some of the hydrochloric acid solution (4.8) to the reservoir, and adjust the flow rate to 10 to 15 ml per minute. If the flow cannot be adjusted to this rate, empty the column and repeat the preparation.

Pass by suction 20 ml of water through the column and follow with 20 ml of the ammonium hydroxide solution (4.13) and then 20 ml of water. Combine the last two eluates and test for absence of aluminium salts by adjusting the pH of the solution until faintly ammoniacal. If aluminium hydroxide precipitates on standing, pass 20 ml of the hydrochloric acid solution (4.7) and then 20 ml of water through the column. Repeat the treatment with 20 ml of the ammonium hydroxide solution (4.13) and 20 ml of water, testing the ammoniacal eluates for absence of aluminium salts as before.

If aluminium hydroxide still precipitates, pass some of the hydrochloric acid solution (4.6) through the column for 1 h without suction and then wash with 50 ml of water. Pass 20 ml of the ammonium hydroxide solution (4.13) and 20 ml of water through the column and test these eluates for absence of aluminium salts.

Repeat this sequence of washing until there is no evidence of aluminium salts being eluted from the column. Finally, wash with 30 ml of the hydrochloric acid solution (4.8).

When the tube is not in use, immerse the lower part in water and fit a rubber bung to the reservoir.

6 Sampling

Select and prepare the samples as specified in ISO/R 377.

7 Procedure

7.1 Test portion

Take a test portion according to the anticipated sulphur content as follows :

a) for sulphur contents up to 0,005 % (m/m), weigh, to the nearest 0,001 g, two test portions, each of approximately 10 g;

b) for sulphur contents of 0,005 % up to 0,05 % (m/m), weigh, to the nearest 0,001 g, a test portion of approximately 10 g;

c) for sulphur contents greater than 0,05 % (m/m), select an amount of test portion such that the sulphur to be determined does not exceed 0,005 g, and weigh, to the nearest 0,001 g.

NOTE — Ideal conditions for the operation of this method require a knowledge of the approximate sulphur content of the test portion. If this is not known, a determination by the combustion technique should be made in order to establish the optimum mass of the test portion and the correct amount of barium chloride required for precipitation.

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7.2 Blank test

With each batch of test portions, carry out a blank test under identical conditions, using the specified amounts of reagents used in the determination, but omitting the test portion.

In the determination of sulphur contents below 0,005 % (m/m), for which two 10 g test portions are used, two blank tests under identical conditions shall be carried out (see 7.3.5).

7.3 Determination

7.3.1 Dissolution of the test portion

Place the test portion (7.1) in a dry conical flask (5.1) for the oxidizing attack.

7.3.1.1 Samples soluble in dilute nitric acid

Place 1 ml of the bromine (4.2) in the conical flask (5.1) and connect the condenser (5.2). Add slowly 50 ml of the nitric acid solution (4.4) in order to control the reaction as far as possible.

Add slowly a further 50 ml of the nitric acid solution (4.4) and when the emission of fumes has ceased, rinse down the inner walls of the condenser with small volume of water, collecting the washings in the conical flask.

When dissolution is complete, heat the solution to boiling until the condensing vapours just reach the first bulbs of the condenser. Allow to cool.

After 5 to 6 min, pour 50 ml of water through the condenser into the conical flask (5.1). Disconnect the conical flask from the condenser, transfer quantitatively the contents to a 500 ml beaker and wash the flask walls with water.

7.3.1.2 Samples insoluble in dilute nitric acid

Place 1 ml of the bromine (4.2) in the conical flask (5.1) and connect the condenser (5.2). Add slowly 100 ml of the nitric acid solution (4.4).

Add 50 ml of the hydrochloric acid (4.5), in small amounts, following the directions applicable to samples soluble in dilute nitric acid.

When the emission of fumes has ceased, rinse down the inner walls of the condenser with a small volume of water and collect the washings in the conical flask.

When dissolution is complete, heat the solution until the condensing vapours just reach the first bulbs of the condenser. Allow to cool.

After 5 to 6 min, pour 50 ml of water through the condenser into the conical flask (5.1). Disconnect the conical flask from the condenser, transfer quantitatively the contents to a 500 ml beaker and wash the flask walls with water.

7.3.2 Addition of sulphate

Add from a burette 10,0 ml of the sulphuric acid solution (4.16) to each test portion (7.1) and also to the solution for the blank test (7.2).

Add 120 ml of the perchloric acid (4.9) and then a few drops of the hydrofluoric acid (4.11).

NOTE — In the case of high silicon steels, further dropwise additions of hydrofluoric acid may be required to facilitate subsequent filtration. The dissolution of alloy steels containing tungsten, niobium, tantalum, titanium and molybdenum may also be facilitated by similar additions of hydrofluoric acid.

For samples with a high chromium content (for example stainless steels), add a further 50 ml of perchloric acid (4.9).

Heat to emission of abundant white fumes. Cover with a dry watch glass and continue boiling until carbonaceous matter is completely decomposed.

7.3.3 Removal of chromium (if necessary)

If the chromium content of the solution is greater than 0,005 g, remove the chromium by the following procedure.

Continue fuming until the chromium is oxidized. Add slowly 5 ml of the hydrochloric acid solution (4.5) and continue heating until the residual chromium is re-oxidized. Repeat the treatment with hydrochloric acid followed by intermediate fuming, until chromyl chloride fumes are no longer evolved.

7.3.4 Reduction of chromium and filtration

Add 200 ml of hot water. Reduce any hexavalent chromium remaining from the volatilization, or present in the test portion, by making dropwise additions of the iron(II) perchlorate solution (4.15) and filter through a 12,5 cm close texture filter paper into an 800 ml beaker. Carefully wash the beaker and paper with warm perchloric acid solution (4.10). Discard the filter.

NOTE — Samples giving large hydrolysis residues (for example niobium, tungsten, etc.) may be difficult to filter. In such cases, filtration may be simplified by using a test portion of 12,5 g instead of 10,0 g required for the determination and then obtaining a 10 g equivalent aliquot by making the solution up to 500 ml and collecting 400 ml by filtration.

The volume of solution should be 500 to 600 ml; if the volume is greater, concentrate the solution.

7.3.5 Chromatographic separation of sulphate

Place the adsorption column (5.3) in the suction filtration flask. Wash the column with 30 ml of water to remove any ammonium hydroxide solution remaining from the previous elution. Acidify the column with 10 ml of the hydrochloric acid solution (4.8). Discard the eluate.

Quantitatively transfer the test solution to the column, drawing it through the column at a flow rate not exceeding 10 ml per minute, and always maintaining some solution above the alumina.

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NOTE — In the determination of sulphur contents below 0,005 %, for which two test portions of 10 g each are used, pass both solutions through the same column using the same procedure as for a single test portion. (This combines the sulphur from the two separate portions, to produce one test portion equivalent to one of 20 g.)

Wash each beaker with two 25 ml portions of the hydrochloric acid solution (4.8) transferring these washings to the column and maintaining the same flow rate. Repeat the washing twice, using 20 ml of water each time, and transfer the washings to the column.

Carry out the two blank tests (7.2) under identical conditions, but omitting the test portion, and pass both solutions through the same column.

Wash the beaker with two 25 ml portions of the hydrochloric acid solution (4.8) transferring these washings to the column and maintaining the same flow rate. Repeat the washing twice, using 20 ml of water each time, and transfer the washings to the column.

Remove the adsorption column from the suction flask and rinse the outer walls of the lower part of the column with water.

7.3.6 Elution with ammonium hydroxide

Place a 250 ml beaker under the column, so that the inner wall of the beaker is in contact with the lower end of the column. Add to the column 15 ml of the ammonium hydroxide solution (4.13) allowing it to flow through by gravity. Then add 40 ml of the ammonium hydroxide solution (4.14), allowing it to flow completely into the beaker.

Finally run 30 to 40 ml of water through the column, collecting this in the beaker.

7.3.7 Precipitation of sulphates and weighing

Neutralise the combined eluates with some of the hydrochloric acid solution (4.7) in the presence of a few drops of the methyl orange solution (4.18), add 2 ml excess of the acid and evaporate the solution to approximately 50 ml. Filter through a 9 cm diameter filter paper of close texture collecting the filtrate in a 250 ml beaker and wash the original beaker and the filter paper four times with small volumes of water.

Whilst constantly stirring the filtrate, add dropwise from a burette the amount of barium chloride solution (4.17) which is in stoichiometric relationship with the expected sulphur content of the test portion together with that of the added sulphate solution. Allow to stand for 1 h, and then add, from the same burette, 20,0 ml excess of the barium chloride solution (4.17). Stir the solution, cover with a watch-glass and allow to stand for about 12 h.

Filter through a 9 cm diameter non-hardened, close texture filter paper or alternatively through a small, tightly packed, ashless paper pulp pad. Wash six times with 5 to 10 ml portions of cold water.

Put the filter and precipitate in a platinum crucible, which has been previously heated to 800 °C, cooled in a desiccator and weighed to the nearest 0,1 mg. Dry and oxidize at as low a temperature as possible (not above 550 °C) until carbonaceous matter is removed, and finally heat to 800 °C. Cool in a desiccator and weigh to the nearest 0,1 mg.

8 Expression of results

The sulphur content, S, expressed as a percentage by mass, is given by the formula

$$0{,}137\,3 \times \frac{m_1 - m_2}{m_0} \times 100$$

where

m_1 is the mass, in grams, of barium sulphate obtained from the test portion;

m_2 is the mass, in grams, of barium sulphate obtained in the blank test;

m_0 is the mass, in grams, of the test portion;

0,137 3 is the conversion factor from barium sulphate ($BaSO_4$) to sulphur (S).

9 Test report

The test report shall contain the following particulars :

a) reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the test;

d) any operations not included in this International Standard which are regarded as optional.

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