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Metallurgical-grade fluorspar — Determination of antimony content — Solvent extraction atomic absorption spectrometric method

Spaths fluor utilisables dans l'industrie métallurgique — Dosage de l'antimoine — Méthode par spectrométrie d'absorption atomique après extraction

Reference number
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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 approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 9504 was prepared by Technical Committee ISO/TC 175, *Fluorspar.*

Annex A of this International Standard is for information only.

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Metallurgical-grade fluorspar — Determination of antimony content — Solvent extraction atomic absorption spectrometric method

1 Scope

This International Standard specifies a solvent extraction atomic absorption spectrometric method for the determination of the antimony content of metallurgical-grade fluorspar.

The method is applicable to products having an antimony content equal to or greater than 0,001 % (m/m).

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 565 : 1983, *Test sieves — Woven metal wire cloth, perforated plate and electroformed sheet — Nominal sizes of openings.*

ISO 4282 : 1977, *Acid-grade fluorspar — Determination of loss in mass at* 105 °C.

3 Principle

A test portion is decomposed by a mixture of nitric, hydrofluoric and perchloric acids. After evaporation to fumes of sulfuric acid, the salts are dissolved in hydrochloric acid.

Antimony is extracted from a dilute hydrochloric acid solution of the decomposed test portion, containing ascorbic acid and potassium iodide, into a solution of tri-*n*-octylphosphine oxide in 4-methyl-2-pentanone.

The 4-methyl-2-pentanone extract is aspirated into the air/acetylene flame of an atomic absorption spectrometer. Spectral energy at 217,6 nm from an antimony hollow-cathode lamp is passed through the flame and the absorbance is measured.

4 Reagents

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

4.1 4-methyl-2-pentanone, for use as a spectrometer-zeroing solution.

4.2 Hydrochloric acid, diluted 1 + 1.

Dilute one volume of hydrochloric acid (ϱ 1,18 g/ml) with one volume of water.

4.3 Hydrochloric acid, diluted 1 + 9.

Dilute one volume of hydrochloric acid (ϱ 1,18 g/ml) with nine volumes of water.

4.4 Nitric acid, ϱ 1,38 g/ml.

4.5 Perchloric acid, ϱ 1,54 g/ml, about 60 % (m/m) solution.

WARNING — Perchloric acid vapour may cause explosions in the presence of ammonia, nitrous fumes or organic matter in general.

4.6 Hydrofluoric acid, ϱ 1,13 g/ml, about 40 % (m/m) solution, or ϱ 1,185 g/ml, about 48 % (m/m) solution.

WARNING — Very toxic by inhalation, in contact with skin and if swallowed. Causes severe burns.

Keep container tightly closed in a well-ventilated place. In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

Wear suitable protective clothing and gloves. In case of accident or feeling unwell, seek medical advice immediately (show the label where possible).

4.7 Sulfuric acid, diluted 1 + 1.

Pour slowly and with care one volume of sulfuric acid (ϱ 1,84 g/ml) into one volume of water.

4.8 Hydrochloric/nitric acid mixture (aqua regia).

Mix three volumes of hydrochloric acid (ϱ 1,18 g/ml) with one volume of nitric acid (4.4).

The solution shall be prepared immediately before use.

4.9 Potassium iodide/L(+)-ascorbic acid, solution in hydrochloric acid.

Dissolve 30 g of potassium iodide and 10 g of L(+)-ascorbic acid in 100 ml of 1+9 hydrochloric acid solution (4.3).

Prepare a fresh potassium iodide/ascorbic acid solution each day.

4.10 Tri-*n*-octylphosphine oxide, 50 g/l solution in 4-methyl-2-pentanone.

Dissolve 5 g of tri-*n*-octylphosphine oxide in 100 ml of 4-methyl-2-pentanone (4.1).

4.11 Antimony, stock standard solution corresponding to 0,500 0 g of Sb per litre.

Weigh, to the nearest 0,1 mg, 0,500 0 g of antimony (purity 99,9 % min.) and dissolve in 20 ml of aqua regia (4.8). Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with 1+1 hydrochloric acid (4.2) and mix.

1 ml of this standard solution contains 0,500 0 g of Sb.

4.12 Antimony, standard solution corresponding to 0,050 0 g of Sb per litre.

Pipette 10 ml of the antimony stock standard solution (4.11) into a 100 ml one-mark volumetric flask, dilute to the mark with 1+1 hydrochloric acid (4.2) and mix.

1 ml of this standard solution contains 0,050 0 mg of Sb.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Atomic absorption spectrometer, *equipped with an* air/acetylene burner and an antimony hollow-cathode lamp.

5.2 Platinum dish, capacity about 100 ml.

5.3 Electric oven, capable of being maintained at 105 °C ± 2 °C.

5.4 Separating funnels, capacity 100 ml.

6 Test sample

Use the residue from the determination of the loss in mass at 105 °C (see ISO 4282) to prepare the test sample.

NOTE — ISO 4282, although specified for acid-grade fluorspar, is equally applicable to metallurgical-grade fluorspar.

7 Procedure

WARNING — Due to the danger of serious accidents when perchloric acid is used, it should be handled in a special fume cupboard with an absorber unit in the exhaust.

7.1 Test portion

Grind several grams of the test sample (see clause 6) in an agate mortar until it all passes a 63 µm mesh sieve (see ISO 565). Dry the ground material for 2 h in the oven (5.3), maintained at 105 °C ± 2 °C, allow to cool in a desiccator and weigh, to the nearest 1 mg, about 0,5 g into the platinum dish (5.2).

7.2 Blank test

Carry out a blank test simultaneously with the determination, following the same procedure and using the same quantities of all reagents as used for the determination, but omitting the test portion.

7.3 Calibration and determination

7.3.1 Preparation of calibration solutions

Into each of a series of six 100 ml separating funnels (5.4), place the volumes of the antimony standard solution (4.12), 1+1 hydrochloric acid (4.2) and water shown in table 1.

Table 1 — Composition of calibration solutions

Antimony standard solution (4.12) ml	Corresponding mass of Sb mg	1+1 hydrochloric acid (4.2) ml	Water ml
0*)	0	10	25
1,0	0,050	9	25
2,0	0,100	8	25
3,0	0,150	7	25
4,0	0,200	6	25
5,0	0,250	5	25

*) Zero calibration solution.

Treat each of these solutions as follows:

Add 15 ml of potassium iodide/L(+)-ascorbic acid solution (4.9), then, using a pipette, add 10 ml of tri-*n*-octylphosphine oxide solution (4.10). Shake the funnel for 1 min. Allow the organic layer to settle, discard the aqueous layer, and draw off the organic layer into a test tube with a ground-glass stopper.

7.3.2 Preparation of the test solution

Transfer the test portion (7.1) to a platinum dish (5.2). Add 5 ml of nitric acid (4.4), 10 ml of hydrofluoric acid (4.6) and 10 ml of perchloric acid (4.5). Heat until dissolution is complete and evaporate the solution to white fumes of perchloric acid.

Add 10 ml of sulfuric acid (4.7). Evaporate just till the appearance of dense white fumes of sulfuric acid following the evolution of perchloric acid fumes, and heat for a further 8 min to 10 min. Remove the platinum dish from the hotplate and allow to cool. Add 10 ml of 1 + 1 hydrochloric acid (4.2), cover the dish with a watch-glass, heat for several minutes and then allow to cool.

Transfer the solution to a 100 ml separating funnel (5.4) with 25 ml of water. Add 15 ml of potassium iodide/L(+)-ascorbic acid solution (4.9), then, using a pipette, add 10 ml of the tri-*n*-octylphosphine oxide solution (4.10) and carry out the extraction procedure specified in 7.3.1, last paragraph.

7.3.3 Adjustment of atomic absorption spectrometer

Set the wavelength to 217,6 nm. Fit the air/acetylene burner and, in accordance with the manufacturer's instructions, light the appropriate flame. After 10 min preheating of the burner, adjust fuel and burner to obtain maximum absorbance while aspirating the highest-concentration calibration solution (see table 1).

Aspirate 4-methyl-2-pentanone (4.1) and the highest-concentration calibration solution alternately until the absorbance reading does not drift and then set the initial reading for 4-methyl-2-pentanone to zero absorbance.

7.3.4 Spectrometric measurements

Aspirate 4-methyl-2-pentanone (4.1) until the initial reading is again obtained (see 7.3.3). Aspirate the calibration solutions (7.3.1) and the test solutions in order of increasing absorption, starting with the blank test solution (see 7.2), and aspirating the zero calibration solution (see table 1) and the test solution at the appropriate points in the series. When a stable response is obtained for each solution, record the reading. Aspirate 4-methyl-2-pentanone between each solution. Repeat the measurements at least twice more.

7.3.5 Plotting the calibration graph

Obtain the net absorbance of each calibration solution by subtracting the absorbance of the zero calibration solution (see table 1). Prepare the calibration graph by plotting the averages of the net absorbance of antimony obtained for the calibration solutions against the concentrations of antimony.

8 Expression of results

8.1 Method of calculation

Using the calibration graph (see 7.3.5), determine the concentration of antimony in the test solution corresponding to the net absorbance of this solution.

The antimony content of the sample, expressed as a percentage by mass of Sb, is given by the formula

$$\frac{\varrho(\text{Sb})_1 - \varrho(\text{Sb})_0}{m} \times 100$$

where

$\varrho(\text{Sb})_0$ is the concentration of antimony, expressed in milligrams per 10 ml, in the blank test solution, corresponding to the net absorbance read off the calibration graph (see 7.3.5);

$\varrho(\text{Sb})_1$ is the concentration of antimony, expressed in milligrams per 10 ml, in the test solution, corresponding to the net absorbance read off the calibration graph (see 7.3.5);

m is the mass, in milligrams, of the test portion (see 7.1).

8.2 Precision

See informative annex A.

9 Test report

The test report shall include the following particulars:

a) all details necessary for the identification of the sample;

b) the method used (a reference to this International Standard);

c) the results and the units in which they have been expressed;

d) any unusual features noted during the determination;

e) details of any operation not included in this International Standard or in the International Standards to which reference is made, as well as details of any operation regarded as optional.

Annex A
(informative)

Interlaboratory test results

A.1 General

The method was tested using three samples of metallurgical-grade fluorspar. The tests were conducted at eight laboratories in Japan. The results, indicating good correlation, are listed in table A.1.

A.2 Confirmation of non-interference of sulfuric acid and calcium

To determine the influence of sulfuric acid and calcium on the extraction of antimony, further tests were carried out with a test portion consisting of 100 µg of antimony, adding different amounts of sulfuric acid and calcium.

The results are given in figures A.1 and A.2. The figures show that neither sulfuric acid nor calcium interferes with the determination of 100 µg of antimony.