INTERNATIONAL
STANDARD

ISO
9779

First edition
1990-03-15

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

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

Reference number
ISO 9779 : 1990 (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 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 9779 was prepared by Technical Committee ISO/TC 175, *Fluorspar.*

Annex A of this International Standard is for information only.

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Case postale 56 • CH-1211 Genève 20 • Switzerland
Printed in Switzerland

Metallurgical-grade fluorspar — Determination of lead 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 lead content of metallurgical-grade fluorspar.

The method is applicable to products having lead contents in the range 0,000 6 % (m/m) to 0,01 % (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 dryness, the salts are dissolved in hydrochloric acid.

Lead is extracted from a dilute hydrochloric acid solution of the decomposed test portion, containing ascorbic acid and sodium 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 283,3 nm from a lead 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 Nitric acid, diluted 1 + 1.

Dilute one volume of nitric acid (4.4) with one volume of water.

4.6 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.

4.7 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).

4.8 Sodium iodide/L(+)-ascorbic acid, solution in hydrochloric acid.

Dissolve 41,5 g of sodium iodide and 10 g of L(+)-ascorbic acid in 100 ml of 1+9 hydrochloric acid (4.3). Prepare a fresh sodium iodide/ascorbic acid solution each day.

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

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

4.10 Lead, stock standard solution corresponding to 0,200 0 g of Pb per litre.

Weigh, to the nearest 0,1 mg, 0,200 0 g of lead (purity 99,9 % minimum) and dissolve in 30 ml of 1+1 nitric acid (4.5). Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 0,200 0 mg of Pb.

4.11 Lead, standard solution corresponding to 0,020 0 g of Pb per litre.

Pipette 10 ml of the lead stock standard solution (4.10) into a 100 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 0,020 0 mg of Pb.

4.12 Matrix matching solution.

Weigh out 10 g of calcium carbonate and dissolve it in 30 ml of 1+1 hydrochloric acid (4.2). Transfer the solution quantitatively to a 100 ml one-mark volumetric flask, dilute to the mark with 1+9 hydrochloric acid (4.3) and mix.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Atomic absorption spectrometer, equipped with an air/acetylene burner and a lead 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 1,0 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 lead standard solution (4.11), matrix matching solution (4.12) and water shown in table 1.

Table 1 — Composition of calibration solutions

Lead standard solution (4.11) ml	Corresponding mass of Pb mg	Matrix matching solution (4.12) ml	Water ml
0*)	0	10	25
1,0	0,020	10	24
2,0	0,040	10	23
3,0	0,060	10	22
4,0	0,080	10	21
5,0	0,100	10	20

*) *Zero calibration solution.*

Treat each of these solutions as follows:

Add 10 ml of sodium iodide/L(+)-ascorbic acid solution (4.8), then, using a pipette, add 10 ml of tri-*n*-octylphosphine oxide solution (4.9) and 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 (4.7) and 10 ml of perchloric acid (4.6). Heat until dissolution is complete and evaporate the solution to white fumes of perchloric acid and then to dryness.

Add 10 ml of 1 + 1 hydrochloric acid (4.2) and heat until drying is complete. Remove the platinum dish from the plate 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 10 ml of sodium iodide/L(+)-ascorbic acid solution (4.8), then, using a pipette, add 10 ml of the tri-*n*-octylphosphine oxide solution (4.9) 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 283,3 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 and determination

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 lead obtained for the calibration solutions against the concentrations of lead.

8 Expression of results

8.1 Method of calculation

Determine the concentration of lead in the test solution using the calibration graph (see 7.3.5).

The lead content of the sample, expressed as a percentage by mass of Pb, is given by the formula

$$\frac{\varrho(\mathrm{Pb})_1 - \varrho(\mathrm{Pb})_0}{m} \times 100$$

where

$\varrho(\mathrm{Pb})_0$ is the concentration of lead, 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);

$\varrho(\mathrm{Pb})_1$ is the concentration of lead, 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

Comparative analyses carried out in eight laboratories on four samples gave the results shown in table A.1.

Table A.1 — Results of interlaboratory tests

Pb [ppm (m/m)]

Sample / Laboratory	Thailand-1			Thailand-2			Vergenoeg			China		
	x	$\bar{x}$	σ_x	x	$\bar{x}$	σ_x	x	$\bar{x}$	σ_x	x	$\bar{x}$	σ_x
1	23 25	24	1,4	41 39	40	1,4	7 6	6,5	0,7	2 2	2	0
2	25 26	25,5	0,7	43 44	43,5	0,7	7 7	7	0	2 2	2	0
3	25 24	24,5	0,7	44 43	43,5	0,7	7 6	6,5	0,7	2 3	2,5	0,7
4	26 23	24,5	1,5	47 46	46,5	0,7	7 6	6,5	0,7	1 3	2	1,4
5	24 26	25	1	43 40	41,5	2,1	7 6	6,5	0,7	4 2	3	1,4
6	28 26	27	1	44 42	43	1,4	7 7	7	0	2 2	2	0
7	19 21	20	1	44 38	41	4,2	4 5	4,5	0,7	2 3	2,5	0,7
8	24 23	23,5	0,7	42 44	43	1,4	6 7	6,5	0,7	2 2	2	0
$\bar{\bar{x}}$	24,2			42,8			6,4			2,2		
σ_r	1,3			1,9			0,6			0,8		
σ_R	2,3			2,4			0,9			0,6		
CV	9,5			5,6			14,1			27,3		

where

x is the result of a determination;

$\bar{x}$ is the mean of the determinations made by a particular laboratory on a particular sample;

σ_x is the standard deviation for these determinations, given by the equation:

$$\sigma_x = \sqrt{\frac{1}{n-1}\Sigma(x-\bar{x})^2}$$

in which n is the number of determinations;

$\bar{\bar{x}}$ is the overall mean, for a particular sample, of the means $\bar{x}$, given by the equation:

$$\bar{\bar{x}} = \frac{1}{p}\Sigma\bar{x}$$

in which p is the number of laboratories involved;

σ_r is the repeatability standard deviation, given by the equation:

$$\sigma_r = \sqrt{\frac{1}{p}\Sigma\sigma_x^2}$$

σ_R is the reproducibility standard deviation, given by the equation:

$$\sigma_R = \sqrt{\frac{1}{p-1}\Sigma(\bar{x}-\bar{\bar{x}})^2 - \frac{\sigma_r^2}{n} + \sigma_r^2}$$

CV is the coefficient of variation, given by the equation:

$$\mathrm{CV} = \frac{\sigma_R}{\bar{\bar{x}}} \times 100$$