

INTERNATIONAL STANDARD

ISO
9505

First edition
1992-01-15

All grades of fluorspar — Determination of arsenic content — Silver diethyldithiocarbamate spectrometric method

iTeh STANDARD PREVIEW

*Tous les spaths fluor — Dosage de l'arsenic — Méthode spectrométrique
au diéthylidithiocarbamate d'argent*

ISO 9505:1992

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Reference number
ISO 9505:1992(E)

Foreword

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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 9505 was prepared by Technical Committee ISO/TC 175, *Fluorspar*.

Annex A of this International Standard is for information only.

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

Printed in Switzerland

All grades of fluorspar — Determination of arsenic content — Silver diethyldithiocarbamate spectrometric method

1 Scope

This International Standard specifies a silver diethyldithiocarbamate spectrometric method for the determination of the arsenic content of all grades of fluorspar.

The method is applicable to products having arsenic (As) contents which are equal to or greater than 0,000 1 % (*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 565:1990, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings*.

ISO 8868:1989, *Fluorspar — Sampling and sample preparation*.

3 Principle

A test portion is dissolved in a mixture of nitric acid, sulfuric acid, hydrochloric acid and saturated bromine water and evaporated to the stage where the sulfuric acid just commences fuming. The arsenic present is reduced by zinc in a hydrochloric acid medium, to arsine. The arsine is absorbed in a solution of silver diethyldithiocarbamate. The purplish-red colour produced by the colloiddally dispersed silver is measured in a spectrometer at a wavelength of approximately 530 nm.

4 Reagents

All the reagents, and the zinc in particular, shall be free from arsenic or have a very low arsenic content. Only distilled water, or water of equivalent purity, shall be used in the analysis.

4.1 Hydrochloric acid, ρ approximately 1,18 g/ml, about 35 % (*m/m*) solution.

4.2 Nitric acid, ρ approximately 1,38 g/ml, about 60 % (*m/m*) solution.

4.3 Sulfuric acid, diluted 1 + 2, ρ approximately 1,34 g/ml, about 44 % (*m/m*) solution.

Add 1 volume of sulfuric acid, ρ approximately 1,84 g/ml, to 2 volumes of water. Cool the solution while mixing.

4.4 Sulfuric acid, diluted 1 + 10, ρ approximately 1,10 g/ml, about 15 % (*m/m*) solution.

Add 1 volume of sulfuric acid, ρ approximately 1,84 g/ml, to 10 volumes of water. Cool the solution while mixing.

4.5 Sodium hydroxide, approximately 40 g/l solution.

4.6 Bromine water, saturated solution.

4.7 Potassium iodide.

4.8 Tin(II) chloride, hydrochloric acid solution.

Dissolve 40 g of tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in hydrochloric acid (4.1) and dilute to 100 ml with the same hydrochloric acid.

Store the solution in an air-tight container.

4.9 Lead(II) acetate, 120 g/l solution.

Dissolve 12 g of lead(II) acetate trihydrate $[\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}]$ in water containing one or two drops of glacial acetic acid and dilute to 100 ml.

4.10 Zinc, granular form.

4.11 Silver diethyldithiocarbamate $[\text{Ag}(\text{DDTC})]$, 2,5 g/l solution in chloroform.

Dissolve 0,25 g of silver diethyldithiocarbamate $(\text{C}_5\text{H}_{10}\text{NS}_2\text{Ag})$ and 0,1 g of brucine dihydrate $(\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4 \cdot 2\text{H}_2\text{O})$ in 100 ml of chloroform and mix well.

4.12 Arsenic, standard solution, corresponding to 100 mg of As per litre.

Weigh, to the nearest 0,1 mg, 0,132 0 g of arsenic trioxide (As_2O_3) and dissolve it in 2 ml of sodium hydroxide solution (4.5). Dilute with water to 500 ml, add 1 + 10 sulfuric acid (4.4) to make the solution slightly acidic and mix. Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 100 µg of As.

4.13 Arsenic, standard solution, corresponding to 1 mg of As per litre.

Transfer 10,0 ml of standard arsenic solution 4.12 to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

Prepare this solution immediately before use.

1 ml of this standard solution contains 1 µg of As.

5 Apparatus

All the glass containers used for the determination of arsenic shall be washed with hot concentrated sulfuric acid, taking the necessary precautions, rinsed thoroughly with water and dried completely.

Ordinary laboratory apparatus and

5.1 Apparatus for the liberation and total absorption of arsine, made of arsenic-free glass or arsenic-free plastic.

A suitable apparatus, shown in figure 1, is made up of the elements described in 5.1.1 to 5.1.4.

5.1.1 Conical flask, 100 ml capacity, for the liberation of the arsine.

5.1.2 Glass wool, which has been soaked in lead(II) acetate solution (4.9) and allowed to drain, in order to absorb any hydrogen sulfide which may be released with the arsine.

5.1.3 Connecting tube.

5.1.4 Absorption tube, containing silver diethyldithiocarbamate solution (4.11) for the absorption of the arsine.

5.2 Spectrometer with a selector for continuous variation of wavelength, fitted with a cell of optical path length 1 cm, or

5.3 Spectrometer with a selector for discontinuous variation of wavelength, fitted with a cell of optical path length 1 cm and with filters giving a maximum transmission at about 530 nm.

5.4 Electric oven, capable of being maintained at a temperature of $105\text{ }^\circ\text{C} \pm 2\text{ }^\circ\text{C}$.

5.5 Polytetrafluoroethylene-coated aluminium dish, of diameter approximately 70 mm and of capacity about 100 ml, or

5.6 Polytetrafluoroethylene dish, of the same diameter and of the same capacity.

5.7 Hotplate, capable of being maintained at a temperature of $225\text{ }^\circ\text{C} \pm 25\text{ }^\circ\text{C}$.

5.8 Steam bath.

Dimensions in millimetres

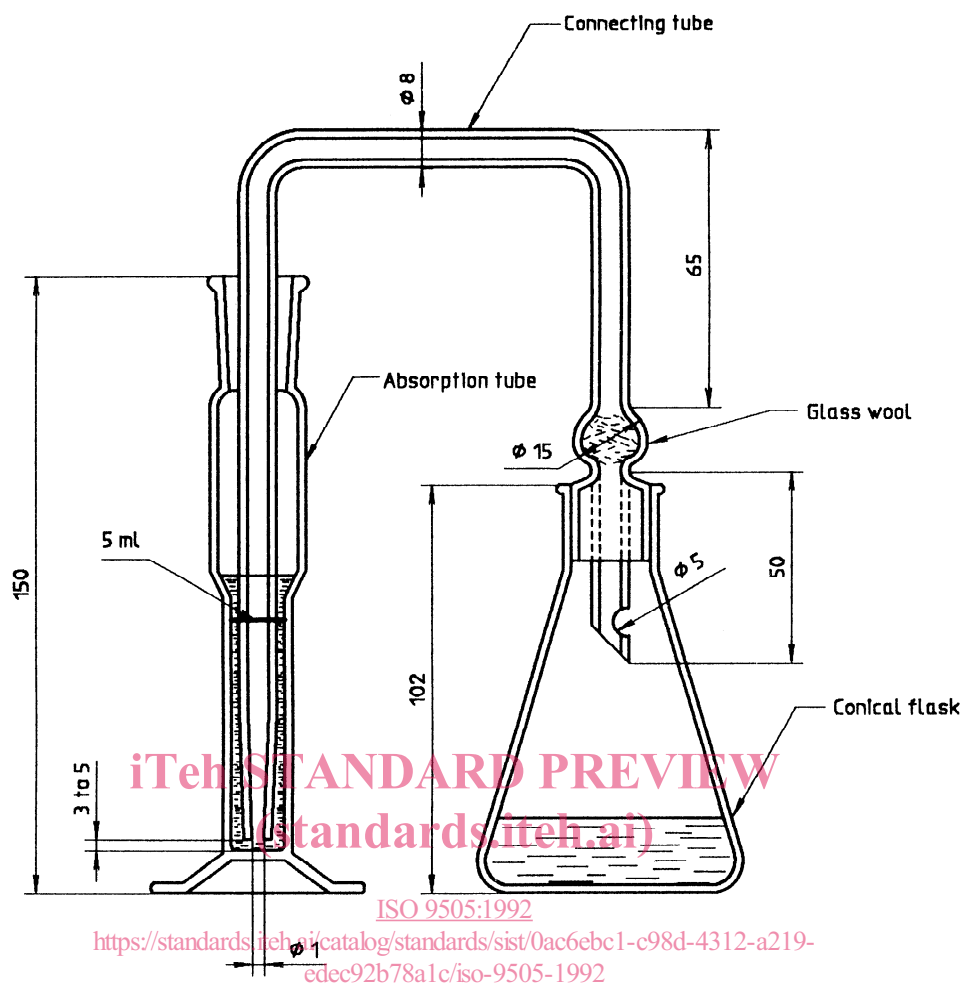


Figure 1 — Typical apparatus for the liberation and absorption of arsine

6 Test sample

Prepare the test sample in accordance with the procedure given in ISO 8868:1989, subclause 9.3.

7 Procedure

7.1 Test portion

Grind several grams of the test sample (clause 6) in an agate mortar until it passes through a $63\ \mu\text{m}$ mesh sieve (see ISO 565). Dry the ground material for 2 h in the oven (5.4) maintained at $105\ \text{°C} \pm 2\ \text{°C}$, allow to cool in a desiccator and weigh, to the nearest 1 mg, about 0,5 g of this sample into the polytetrafluoroethylene-coated aluminium dish (5.5) or the polytetrafluoroethylene dish (5.6).

7.2 Blank test

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

7.3 Preparation of the calibration graph

A calibration graph shall be prepared each time that a new batch of zinc is used and each time that a new solution of silver diethyldithiocarbamate is prepared.

7.3.1 Preparation of calibration solutions

Into each of a series of seven conical flasks (5.1.1), introduce, using pipettes, the volumes of arsenic standard solution 4.13 indicated in table 1.

Table 1 — Composition of calibration solutions

Volume of arsenic standard solution 4.13 ml	Corresponding mass of arsenic µg
0 ¹⁾	0
1	1
3	3
5	5
10	10
15	15
20	20

1) Zero calibration solution.

Dilute the contents of each flask to about 20 ml with water. Add 5 ml of hydrochloric acid (4.1), 3 g of potassium iodide (4.7) and 1 ml of tin(II) chloride solution (4.8) in the order given. Dilute with water to about 40 ml, swirl well and then allow to stand for about 15 min.

Transfer, using a pipette, 5,0 ml of silver diethyldithiocarbamate solution (4.11) to the absorption tube (5.1.4). Add 3 g of granular zinc (4.10) to one of the conical flasks, assemble the apparatus (5.1) immediately and cool the outside of the conical flask. Allow approximately 1 h for the reaction to take place. The arsine is absorbed in the silver diethyldithiocarbamate solution (4.11), producing a purplish-red colour. Repeat for the remaining conical flasks.

7.3.2 Spectrometric measurements

After each arsine liberation and absorption procedure, dilute the silver diethyldithiocarbamate solution remaining in the absorption tube to 5,0 ml with chloroform. Transfer the solution to a cell of optical path length 1 cm. Carry out the measurements using either spectrometer 5.2 at a wavelength of approximately 530 nm, or with spectrometer 5.3 fitted with suitable filters, after having adjusted the instrument, in each case, to zero absorbance against water.

7.3.3 Plotting the calibration graph

Deduct the absorbance of the zero calibration solution from that of each calibration solution. Plot a graph having, for example, the arsenic contents in micrograms in the calibration solutions as abscissae and the corresponding values of the absorbance as ordinates.

7.4 Determination

7.4.1 Preparation of the test solution

Treat the test portion (7.1) in the dish (5.5 or 5.6) as follows:

Add 2 ml of nitric acid (4.2), 5 ml of sulfuric acid (4.3), 6 ml of hydrochloric acid (4.1) and 5 ml of saturated bromine water (4.6). Heat on a steam bath (5.8) in order to eliminate the excess nitric acid and hydrochloric acid. Continue heating until no further smell of acids can be detected. Evaporate on a hotplate (5.7), maintained at a temperature of $225\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$, to the stage where fuming of sulfuric acid only just commences (it is absolutely essential that evaporation is not continued beyond the stage where fuming of the sulfuric acid is just commencing). Cool to room temperature and add about 10 ml of water. Pulverize the contents of the dish with a polytetrafluoroethylene rod and transfer it quantitatively, using about 10 ml of water, to the conical flask (5.1.1) to be used for the liberation of the arsine.

Complete the operations in accordance with the procedure described in 7.3.1.

7.4.2 Spectrometric measurements

Carry out the spectrometric measurements on the test solution (7.4.1) and on the blank test solution (7.2) in accordance with the procedure described in 7.3.2, after having adjusted the instruments to zero absorbance against water.

8 Expression of results

By reference to the calibration graph (7.3.3), determine the masses of arsenic corresponding to the values of the absorbances of the test solution and of the blank test solution.

The arsenic content, expressed as a percentage by mass of As, is given by the formula

$$\frac{m_1 - m_2}{m_0} \times 10^{-4}$$

where

- m_0 is the mass, in grams, of the test portion (7.1);
- m_1 is the mass, in micrograms, of As found in the test solution (7.4);
- m_2 is the mass, in micrograms, of As found in the blank test solution (7.2).

9 Test report

The test report shall include the following particulars:

- a) an identification of the sample;
- b) a reference to this International Standard;
- c) the results and the units in which they are expressed;
- d) any unusual features noted during the determination;
- e) any operation not included in this International Standard or in the International Standards to which reference is made, as well as any operations regarded as optional.

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Annex A (informative)

Precision of the method

Comparative analyses carried out in five laboratories on two samples gave the statistical information shown in table A.1.

Table A.1 — Precision data

Sample		As [% (m/m)]	
		1	2
Mean As content		0,000 31	0,001 13
Standard deviation	of repeatability, σ_r	0,000 04	0,000 06
	of reproducibility, σ_R	0,000 09	0,000 17

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