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Iron ores — Determination of tin — Flame atomic absorption spectrometric method

Minerais de fer — Dosage de l'étain — Méthode par spectrométrie d'absorption atomique dans la flamme

Reference number
ISO 11534:2006(E)

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 11534 was prepared by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This second edition cancels and replaces the first edition (ISO 11534:1998), which has been technically revised. It has been updated to alter the manner in which the precision data are presented.

Iron ores — Determination of tin — Flame atomic absorption spectrometric method

WARNING — This International Standard may involve hazardous materials, operations and equipment. This International Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this International Standard to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard specifies a flame atomic absorption spectrometric method for the determination of the mass fraction of tin in iron ores.

This method is applicable to mass fractions of tin between 0,001 % and 0,015 % in natural iron ores, iron ore concentrates and agglomerates, including sinter products.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 648: *Laboratory glassware — One-mark pipettes*

ISO 1042: *Laboratory glassware — One-mark volumetric flasks*

ISO 3082: *Iron ores —Sampling and sample preparation procedures*

ISO 3696: *Water for analytical laboratory use — Specification and test methods*

ISO 7764: *Iron ores — Preparation of predried test samples for chemical analysis*

3 Principle

The test portion is treated with sulfuric acid and hydrofluoric acid in a platinum crucible. The silica is removed by heating and evaporation. The residue is fused in sodium carbonate/sodium tetraborate flux, and the cooled melt is dissolved in hydrochloric acid.

Iron is reduced by ascorbic acid and potassium iodide, followed by extraction of tin with tri-*n*-octyl phosphine oxide (TOPO) in 4-methyl-2-pentanone (MIBK) solvent.

The tin TOPO/MIBK extract is aspirated into a dinitrogen oxide/acetylene flame and the absorbance of tin is measured at a 286,3 nm resonance line using a tin hollow-cathode lamp. The absorbance values obtained are compared with those obtained from calibration solutions.

4 Reagents

During the analysis, use only reagents of recognized analytical reagent grade, and only water that complies with grade 2 of ISO 3696.

4.1 Sodium carbonate (Na_2CO_3), anhydrous.

4.2 Sodium tetraborate ($Na_2B_4O_7$), anhydrous.

4.3 Iron oxide (Fe_2O_3), of minimum purity 99,9 % (mass fraction) and mass fraction of tin $< 0{,}000\,2$ %.

4.4 Hydrochloric acid, ρ 1,16 g/ml to ρ 1,19 g/ml.

4.5 Hydrochloric acid, ρ 1,16 g/ml to ρ 1,19 g/ml, diluted 1 + 1.

4.6 Hydrochloric acid, ρ 1,16 g/ml to ρ 1,19 g/ml, diluted 2 + 3.

Add 200 ml of hydrochloric acid (4.4) to 300 ml of water and mix.

4.7 Hydrofluoric acid, ρ 1,13 g/ml, 40 % (mass fraction) or ρ 1,19 g/ml, 48 % (mass fraction).

4.8 Sulfuric acid, ρ 1,84 g/ml.

4.9 Sulfuric acid, ρ 1,84 g/ml, diluted 1 + 1.

4.10 Ascorbic acid solution, 200 g/l.

This solution shall be prepared freshly on the day of use.

4.11 Potassium iodide/ascorbic acid solution.

Dissolve 90 g of potassium iodide in water, add 30 g of ascorbic acid and 30 ml of hydrochloric acid (4.4), and dilute with water to 200 ml. This solution shall be freshly prepared just prior to use.

4.12 Tri-*n*-octyl phosphine oxide (TOPO)/4-methyl-2 pentanone (MIBK) solution.

Dissolve 1 g of TOPO in 100 ml of MIBK.

4.13 Tin standard solution, 200 µg Sn/ml.

Dissolve 0,1 000 g of tin metal [purity > 99,5 % (mass fraction)] in a platinum crucible (with cover) with 5 ml of hydrochloric acid (4.4). After cooling, transfer the solution to a 500 ml one-mark volumetric flask, add 200 ml of hydrochloric acid (4.5), and dilute to volume with hydrochloric acid (4.5).

4.14 Tin standard solution, 40 µg Sn/ml.

Transfer 20 ml of tin standard solution (4.13) to a 100 ml one-mark volumetric flask, dilute to volume with hydrochloric acid (4.5) and mix.

4.15 Tin standard solution, 10 µg Sn/ml.

Transfer 5,0 ml of tin standard solution (4.13) to a 100 ml one-mark volumetric flask, dilute to volume with hydrochloric acid (4.5) and mix.

5 Apparatus

Ordinary laboratory apparatus, including one-mark pipettes and one-mark volumetric flasks complying with the specifications of ISO 648 and ISO 1042 respectively, and the following.

5.1 Platinum crucible, of capacity 25 ml to 30 ml.

5.2 Platinum rod.

5.3 Muffle furnace, suitable for heating at 1 000 °C to 1 020 °C.

5.4 Atomic absorption spectrometer, equipped with a dinitrogen oxide/acetylene burner.

WARNING — To avoid possible explosion hazards, follow the manufacturer's instructions for igniting and extinguishing the dinitrogen oxide/acetylene flame. Wear tinted safety glasses whenever the flame is burning.

The atomic absorption spectrometer used in this method shall meet the following criteria.

a) Minimum sensitivity: the absorbance of the most concentrated calibration solution (see 7.4.5) shall be at least 0,13.

b) Graph linearity: the slope of the calibration graph covering the top 20 % of the concentration range (expressed as a change in absorbance) shall not be less than 0,7 of the value of the slope for the bottom 20 % of the concentration range determined in the same way.

c) Minimum stability: the standard deviation of the absorbance of the most concentrated calibration solution and that of the zero calibration solution, each being calculated from a sufficient number of repetitive measurements, shall be less than 1,5 % and 0,5 %, respectively, of the mean value of the absorbance of the most concentrated calibration solution.

The use of a strip chart recorder and/or digital readout device is recommended to evaluate criteria a), b) and c) for all subsequent measurements.

NOTE Instrument parameters may vary with each instrument. The following parameters were successfully used in several laboratories and they can be used as guidelines. A dinitrogen oxide/acetylene flame was used.

Hollow cathode lamp, mA	12,5
Wavelength, nm	286,3
Dinitrogen oxide flow rate, l/min	6,6
Acetylene flow rate, l/min	4,5

In systems where the values shown above for gas flow rates do not apply, the ratio of the gas flow rates may still be a useful guideline.

6 Sampling and samples

6.1 Laboratory sample

For analysis, use a laboratory sample of minus 100 µm particle size which has been taken and prepared in accordance with ISO 3082. In the case of ores having significant contents of combined water or oxidizable compounds, use a particle size of minus 160 µm.

NOTE A guideline on significant contents of combined water and oxidizable compounds is incorporated in ISO 7764.

6.2 Preparation of predried test samples

Thoroughly mix the laboratory sample and, taking multiple increments, extract a test sample in such a way that it is representative of the whole contents of the container. Dry the test sample at 105 °C ± 2 °C, as specified in ISO 7764. (This is the predried test sample.)

7 Procedure

7.1 Number of determinations

Carry out the analysis at least in duplicate in accordance with Annex A, independently, on one predried test sample.

NOTE The expression “independently” means that the second and any subsequent result is not affected by the previous result(s). For the particular analytical method, this condition implies that the repetition of the procedure is carried out either by the same operator at a different time or by a different operator including, in either case, appropriate recalibration.

7.2 Test portion

Taking several increments, weigh, to the nearest 0,000 2 g, approximately 2 g of the predried test sample obtained in accordance with 6.2.

The test portion should be taken and weighed quickly to avoid re-absorption of moisture.

7.3 Blank test and check test

In each run, one blank test and one analysis of a certified reference material of the same type of ore shall be carried out in parallel with the analysis of the ore sample(s) under the same conditions. A predried test sample of the certified reference material shall be prepared as specified in 6.2.

The certified reference material should be of the same type as the sample to be analysed and the properties of the two materials should be sufficiently similar to ensure that, in either case, no significant changes in the analytical procedure will become necessary. Where a certified reference material is not available, a reference material may be used (see 8.2.4).

Where the analysis is carried out on several samples at the same time, the blank value may be represented by one test, provided that the procedure is the same and the reagents used are from the same reagent bottles.

Where the analysis is carried out on several samples of the same type of ore at the same time, the analytical value of one certified reference material may be used.

7.4 Determination

7.4.1 Decomposition of the test portion

Transfer the test portion (7.2) to a crucible (5.1), moisten with a few drops of water, add 2 ml of sulfuric acid (4.9) and 6 ml of hydrofluoric acid (4.7), mix well using a platinum rod (5.2) and wash the rod with water.

Using a gas burner, heat the crucible gently at first, then to white fumes, and continue heating until no fumes are observed. Place the crucible in a muffle furnace (5.3) at 1 000 °C to 1 020 °C for 30 min.

During the first heating, mix the contents periodically to facilitate the digestion of silica.

Cool the crucible and remove the residue on the crucible walls using a platinum rod. Add 1,6 g of sodium carbonate (4.1) and 0,8 g of sodium tetraborate (4.2), mix well with a platinum rod, and heat over a Meker burner for 5 min or until the mixture has partially melted. Add a further 1,6 g of sodium carbonate and 0,8 g of sodium tetraborate and repeat the heating until the fusion is virtually complete, swirling the crucible to remove any residue on its inner walls. Remove from the heat source and swirl until the melt solidifies on the inner walls of the crucible. Place the crucible in a muffle furnace at 1 000 °C to 1 020 °C for 15 min. Cool and place the crucible in a 200 ml beaker. Add 50 ml of hydrochloric acid (4.6), cover the beaker with a watch glass and heat at 90 °C until dissolution of the melt is complete.

NOTE 1 A pressurized air burner or similar, capable of attaining a temperature of 900 °C or more, may be used instead of a Meker burner.

NOTE 2 The crucible may need to be rolled to ensure complete dissolution of the fused melt.

Remove the crucible and rinse it. Cool the solution.

7.4.2 Treatment of the test solution

Add 20 ml of ascorbic acid solution (4.10) and 4 ml of potassium iodide/ascorbic acid solution (4.11) to the test solution (see 7.4.1) and mix. Transfer the solution to a 200 ml separating funnel having a mark indicating 100 ml volume. Dilute to 100 ml with water and mix gently. Add 10,0 ml of TOPO/MIBK solution (4.12). Stopper the funnel and shake vigorously for 30 s. Allow the layers to separate.

Drain the lower aqueous layer. Drain the organic layer through a dry filter paper into a 25 ml one-mark volumetric flask and stopper it. Reserve the solution for atomic absorption measurement. (This solution is the TOPO/MIBK extract.)

7.4.3 Adjustment of atomic absorption spectrometer

Aspirate MIBK between the TOPO/MIBK extracts of each calibration and test solution.

Ensure that the trap and the drain tube are compatible with the MIBK solvent.

After completion of the test work, drain off the MIBK from the trap.

For normal work with aqueous aspirations, dry and fill with water.

Set the wavelength for tin (286,3 nm) to obtain minimum absorbance, and adjust the readout to zero absorbance.

Taking account of appropriate safety precautions, light the dinitrogen oxide/acetylene flame. After 10 min preheating of the burner, aspirate the TOPO/MIBK extract of the calibration solution having highest mass fraction of tin and carefully adjust the fuel flow and burner position to obtain maximum absorbance.

Check that the conditions for zero absorbance have been maintained while aspirating MIBK, and again aspirate the TOPO/MIBK extract for the solution having the highest mass fraction of tin to establish that the absorbance reading is not drifting. Set the reading for MIBK to zero absorbance.

Water in the trap reservoir has to be emptied, dried and replaced with MIBK for aspirating the TOPO/MIBK extract into the flame.

7.4.4 Atomic absorption measurements

Aspirate the TOPO/MIBK extract for the calibration solutions and the test solution in order of increasing concentration, starting with the zero calibration solution and the blank test solution. When stable responses have been obtained, record the readings in absorbance units. Aspirate MIBK between each TOPO/MIBK extract and repeat the measurements twice more.

The reagents used for the preparation of the zero calibration solution should have a sufficiently low mass fraction of tin.

Correct the absorbance values obtained for the calibration solutions by subtracting the absorbance for the zero calibration solution, and prepare a calibration graph by plotting the net absorbance values against micrograms of tin per millilitre. If the graph is substantially linear, subtract the absorbance obtained for the blank test from the absorbance obtained for the test solution and, using the graph, convert the net absorbance value for the test solution to micrograms of tin per millilitre.

7.4.5 Preparation of calibration solutions

Transfer 2,0 g of iron oxide (4.3) to each of six crucibles (5.1). Decompose the iron oxide by following the procedure specified in 7.4.1. After cooling the solution, add the quantities of tin standard solutions (4.14 and 4.15) shown in Table 1 and follow the procedure specified in 7.4.2.

Table 1 — Calibration solutions

Solution number	**Tin standard solution (4.14)** ml	**Tin standard solution (4.15)** ml	**Tin content** µg
0	0	0	0
1	0	2	20
2	2	0	80
3	4	0	160
4	6	0	240
5	8	0	320

8 Expression of results

8.1 Calculation of mass fraction of tin

The mass fraction of tin, w_{Sn}, expressed as a percentage, is calculated to four decimal places, using the equation

$$w_{\mathrm{Sn}} = (\rho_1 - \rho_2) \times 10 \times 10^{-6}/m \times 100 \qquad (1)$$

$$= (\rho_1 - \rho_2) \times 10^{-3}/m$$

where

ρ_1 is the concentration of tin in the final test solution, in micrograms per millilitre;

ρ_2 is the concentration of tin in the blank test solution, in micrograms per millilitre;

m is the mass of the test portion in the final test solution, in grams.

8.2 General treatment of results

8.2.1 Repeatability and permissible tolerances

The precision of this analytical method is expressed by the following regression equations. See Annexes A and B.

$$\sigma_{\mathrm{d}} = 0{,}006\,0X^{0{,}5611} \qquad (2)$$

$$\sigma_{\mathrm{L}} = 0{,}012\,9X + 0{,}000\,1 \qquad (3)$$

$$R_d = 0{,}016\,9X^{0{,}5611} \quad (4)$$

$$P = 0{,}085\,3X + 0{,}000\,4 \quad (5)$$

where

X is the concentration of tin in the sample and is calculated as follows:

- for the within-laboratory Equations (2, 4), the arithmetic mean of the duplicate values;
- for the between-laboratory Equations (3, 5), the arithmetic mean of the final results (8.2.3) of the two laboratories;

σ_d is the independent duplicate standard deviation;

σ_L is the between-laboratories standard deviation;

R_d is the independent duplicate limit;

P is the permissible tolerance between laboratories.

8.2.2 Determination of the analytical result

Having computed the independent duplicate results according to Equation (1), compare them with the independent duplicate limit (R_d), using the procedure given in Annex A, and obtain the final laboratory result μ (see 8.2.3).

8.2.3 Between-laboratories precision

Between-laboratories precision is used to determine the agreement between the final results reported by two laboratories. The assumption is that both laboratories followed the same procedure as described in 8.2.2.

Compute the following quantity:

$$\mu_{1,2} = \frac{\mu_1 + \mu_2}{2} \quad (6)$$

where

μ_1 is the final result reported by laboratory 1;

μ_2 is the final result reported by laboratory 2;

$\mu_{1,2}$ is the mean of the final results.

Substitute $\mu_{1,2}$ for X in Equation (5) and calculate P.

If $|\mu_1 - \mu_2| \leqslant P$, the final results are in agreement.

8.2.4 Check for trueness

The trueness of the analytical method shall be checked by applying it to a certified reference material (CRM) or a reference material (RM) (see the second paragraph of 7.3). Calculate the analytical result (μ) for the RM/CRM using the procedures in 8.2.3, and compare it with the reference or certified value A_c. There are two possibilities:

a) $|\mu_c - A_c| \leqslant C$ in which case, the difference between the reported result and the reference/certified value is statistically insignificant;

b) $|\mu_c - A_c| > C$ in which case, the difference between the reported result and the reference/certified value is statistically significant.

where

μ_c is the final result for the CRM/RM;

A_c is the reference/certified value for the CRM/RM;

C is a value dependent on the type of CRM/RM used.

Certified reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35:2006, *Reference materials — General and statistical principles for certification*.

For a CRM/RM certified by an interlaboratory test programme

$$C = 2\left[\sigma_L^2 + \frac{\sigma_d^2}{n} + V(A_c)\right]^{1/2} \tag{7}$$

where

$V(A_c)$ is the variance of the certified/reference value A_c (= 0 for a CRM/RM certified by only one laboratory);

n is the number of replicate determinations carried out on the CRM/RM.

CRMs certified by only one laboratory should be avoided unless they are known to have an unbiased certified value.

8.2.5 Calculation of final result

The final result is the arithmetic mean of the acceptable analytical values for the test sample, or as otherwise determined by the operations specified in Annex A, calculated to six decimal places and rounded off to the fourth decimal place as follows:

a) where the figure in the fifth decimal place is less than 5, it is discarded and the figure in the fourth decimal place is kept unchanged;

b) where the figure in the fifth decimal place is 5 and there is a figure other than 0 in the sixth decimal place, or when the figure in the fifth decimal place is greater than 5, the figure in the fourth decimal place is increased by one;

c) where the figure in the fifth decimal place is 5 and the figure 0 is in the sixth decimal place, the 5 is discarded and the figure in the fourth decimal place is kept unchanged if it is 0, 2, 4, 6 or 8 and is increased by one if it is 1, 3, 5, 7 or 9.

8.3 Oxide factor

The oxide factor, $w_{\mathrm{SnO_2}}$, expressed as a percent, is given by the following equation:

$$w_{\mathrm{SnO_2}} = 1{,}270\, w_{\mathrm{Sn}} \tag{8}$$

9 Test report

The test report shall include the following information:

a) name and address of the testing laboratory;

b) date of issue of the test report:

c) a reference to this International Standard;

d) details necessary for the identification of the sample;

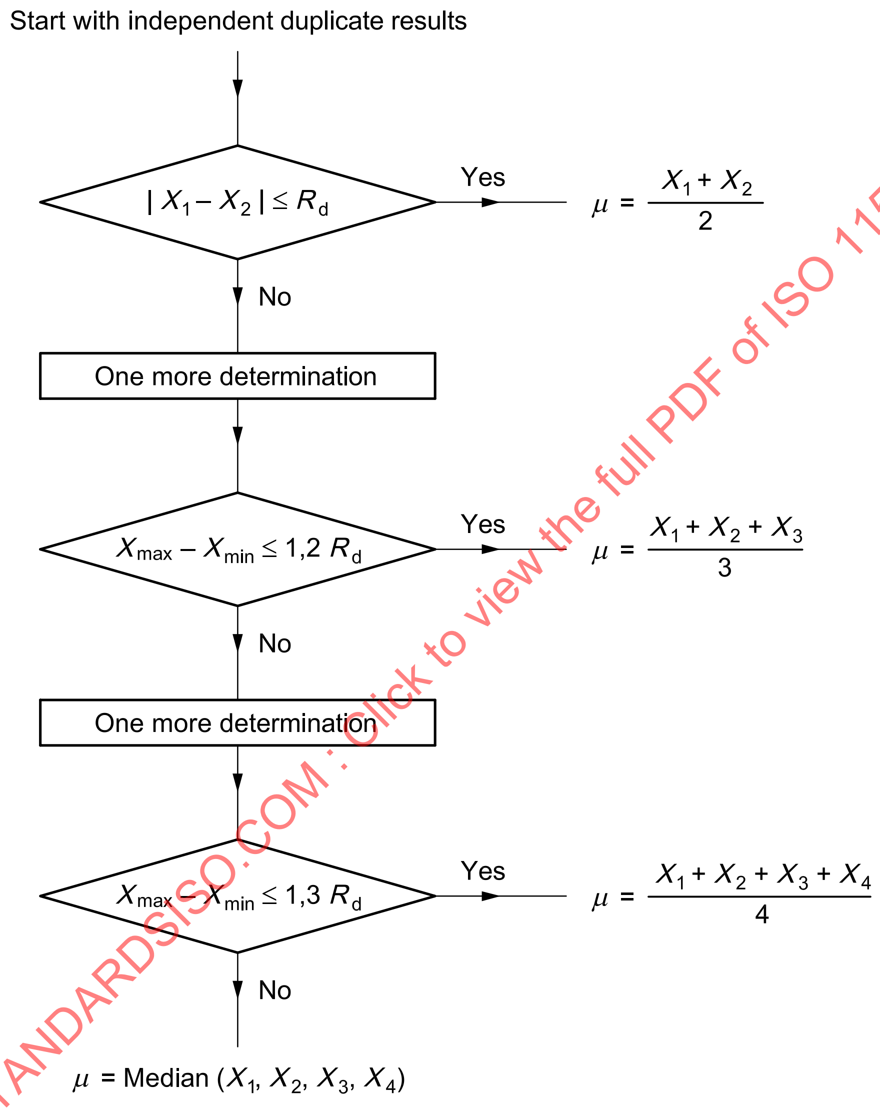
e) result of the analysis;

f) reference number of the result;

g) any characteristics noticed during the determination, and any operations not specified in this International Standard which may have had an influence on the result, for either the test sample or the certified reference material(s).

Annex A
(normative)

Flowsheet of the procedure for the acceptance of analytical values for test samples



R_d: as defined in 8.2.1.