INTERNATIONAL STANDARD

ISO 15353

First edition
2001-03-15

Steel and iron — Determination of tin content — Flame atomic absorption spectrometric method (extraction as Sn-SCN)

Aciers et fontes — Dosage de l'étain — Méthode par spectrométrie d'absorption atomique dans la flamme (extraction comme Sn-SCN)

Reference number
ISO 15353:2001(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 3.

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 International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 15353 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

Annexes A and B of this International Standard are for information only.

Steel and iron — Determination of tin content — Flame atomic absorption spectrometric method (extraction as Sn-SCN)

1 Scope

This International Standard specifies a method for the determination of tin in steel and iron by means of flame atomic absorption spectrometry. The method is applicable to tin contents in the range 0,001 % by mass to 0,1 % by mass.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 648:1977, *Laboratory glassware — One-mark pipettes*.

ISO 1042:1998, *Laboratory glassware — One-mark volumetric flasks*.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*.

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*.

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*.

ISO 5725-3:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 3: Intermediate measures of the precision of a standard measurement method*.

ISO 14284:1996, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition*.

3 Principle

Dissolution of a test portion in hydrochloric and nitric acids. Formation of Sn-SCN complex and extraction of the complex into 4-methyl-2-pentanone (isobutyl methyl ketone).

Aspiration of the organic solution into a dinitrogen monoxide-acetylene flame. Spectrometric measurement of the atomic absorption of the 224,6 nm spectral line emitted by a tin hollow cathode lamp.

High purity tin metal dissolved as standard solution is used as reference material for calibration graphs.

4 Reagents

Use only reagents of recognized analytical grade, unless otherwise stated.

4.1 Water, complying with grade 2 as defined in ISO 3696.

4.2 Hydrochloric acid, HCl, ρ approximately 1,19 g/ml.

4.3 Hydrochloric acid, HCl, diluted 1 + 1.

4.4 Nitric acid, HNO_3 , ρ approximately 1,40 g/ml.

4.5 Formic acid, HCOOH, ρ approximately 1,21 g/ml.

4.6 Hydrochloric acid, HCl, diluted 1 + 24.

4.7 Ascorbic acid, $C_6H_8O_6$.

4.8 Potassium thiocyanate solution.

Dissolve 25 g of potassium thiocyanate (KSCN) in water (4.1), dilute to 50 ml and mix. Prepare the solution shortly before use.

4.9 4-methyl-2-pentanone (isobutyl methyl ketone), $(CH_3)_2 CHCH_2COCH_3$.

4.10 Washing solution.

Dissolve 45 g of ascorbic acid (4.7) and 25 g of potassium thiocyanate in 500 ml of hydrochloric acid (4.6). Prepare the solution shortly before use.

4.11 Tin, standard reference solution.

4.11.1 Stock solution, corresponding to 1 g of tin per litre.

Weigh, to the nearest 0,000 1 mg, approximately 0,25 g of tin metal (minimum 99,9 % by mass). Transfer to a 250 ml beaker and dissolve in 20 ml of hydrochloric acid (4.2) and 5 ml of nitric acid (4.4). Warm gently. Remove from the hot plate immediately after complete dissolution and allow to cool. Transfer the solution to a 250 ml one-mark volumetric flask containing 100 ml hydrochloric acid (4.2). Dilute to the mark with water and mix.

1 ml of this stock solution contains 1 mg of tin.

4.11.2 Standard reference solution A, corresponding to 50 mg of tin per litre.

Transfer 25 ml of the stock solution (4.11.1) to a 500 ml one-mark volumetric flask and add 90 ml of hydrochloric acid (4.2). Dilute to the mark with water and mix.

1 ml of this solution contains 0,05 mg of tin.

4.11.3 Standard solution B, corresponding to 5 mg of tin per litre.

Transfer 25 ml of the standard solution A (4.11.2) to a 250 ml one-mark volumetric flask and add 50 ml of hydrochloric acid (4.2). Dilute to the mark with water and mix.

1 ml of this solution contains 0,005 mg of tin.

4.12 Iron, free from tin (less than 0,000 1 % by mass).

4.13 Solution for optimization of the atomic absorption spectrometer.

Dissolve 4 g of ascorbic acid (4.7) in 40 ml of HCl (4.6). Allow to cool and add 3 ml of the standard stock solution (4.11.1). Proceed exactly as specified in 7.3.2 but transfer the organic phase to a 100 ml volumetric flask, dilute with 4-methyl-2-pentanone (4.9) to the mark and mix. The solution is stable for several weeks if the flask is properly closed.

5 Apparatus

All volumetric glassware shall be grade A, in accordance with ISO 648 or ISO 1042, as appropriate. Use ordinary laboratory apparatus.

5.1 Atomic absorption spectrometer, consisting of a tin hollow cathode lamp fuelled by supplies of acetylene and dinitrogen monoxide sufficiently pure to give a steady, clear, red-feather flame, free from water and oil.

The atomic absorption spectrometer used is deemed satisfactory if, after optimization according to 7.3.5, the limit of detection and characteristic concentration are in reasonable agreement with the values given by the manufacturer and if it meets the precision criteria given in 5.1.1 to 5.1.3. It is also desirable that the instrument conform to the additional performance requirement given in 5.1.4.

5.1.1 Short term stability

The standard deviation of ten measurements of the absorbance of the most concentrated calibration solution shall not exceed 1,5 % of the mean absorbance of the same solution.

5.1.2 Limit of detection

This is determined by taking three times the standard deviation of ten measurements of the absorbance of a solution containing the appropriate element at a concentration level selected to give an absorbance just above that of the zero member. The limit of detection of tin in a matrix similar to the final test portion solution shall be better than 0,1 μg/ml of tin in organic solution.

5.1.3 Graph linearity

The slope of the calibration graph covering the top 20 % of the concentration range (expressed as a change in absorbancy) shall be not less than 0,7 times the value of the slope for the bottom 20 % of the concentration range determined in the same way. For instruments with automatic calibration using two or more standards, it shall be established prior to the analysis, by obtaining absorbance readings, that the above requirements for graph linearity are fulfilled.

5.1.4 Characteristic concentration

The characteristic concentration for tin in a matrix similar to the final test portion solution shall be better than 0,4 μg/ml of tin in organic solution.

5.2 Ancillary equipment, consisting of a strip chart recorder and/or digital readout device recommended to evaluate the criteria listed for 5.1 and for all subsequent measurements.

Scale expansion can be used until the noise observed is greater than the readout error and is always recommended for absorbances below 0,1. If scale expansion has to be used and the instrument does not have the means to read the value of the scale expansion factor, the value can be calculated by measuring a suitable solution with and without scale expansion and simply dividing the signal obtained.

6 Sampling

Carry out sampling in accordance with ISO 14284 or appropriate national standards for steel.

7 Procedure

7.1 Test portion

Weigh, to the nearest 0,000 1 g, a test portion of the sample according to Table 1.

Table 1 — Test portions

Expected tin content % by mass	**Test portion** g
0,001 to 0,025	1
0,025 to 0,05	0,5
0,05 to 0,1	0,25

7.2 Blank test

In parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all the reagents but omitting the test portion.

7.3 Determination

7.3.1 Preparation of the test solution

Place the test portion (see 7.1) in a 250 ml beaker. Add 20 ml of hydrochloric acid (4.3) and 5 ml of nitric acid (4.4) then cover the beaker. Heat gently. After complete dissolution, immediately remove the beaker from the hot plate and allow to cool.

Rinse the lid with water and add 5 ml of formic acid (4.5). Heat gently (without lid) until the reaction has ceased, then immediately remove the beaker from the hot plate. Dilute with 20 ml of hydrochloric acid (4.6).

Add 4 g of ascorbic acid (4.7) and dissolve by gentle heating. Remove immediately from the hot plate and cool to ambient temperature.

7.3.2 Extraction

Transfer the sample solution quantitatively to a 125 ml separating funnel and dilute with hydrochloric acid (4.6) to 60 ml. Add 5 ml potassium thiocyanate solution (4.8) and 10 ml 4-methyl-2-pentanone (4.9). Shake vigorously for 60 s.

Let the phases separate completely. This normally takes approximately 5 min, but in the case of samples containing graphite, or elements that precipitate, it may take up to 15 min to 20 min. Discard the lower aqueous phase.

Add 50 ml of washing solution (4.10). Shake vigorously for 120 s. Let the phases separate completely. Discard the lower aqueous phase. It is not necessary to separate the organic phase quantitatively. Discard approximately 0,5 ml of this together with the aqueous phase. Make sure that all water is removed from the stem of the separation funnel.

Filter the organic phase through a dry rapid filter paper into a dry 10 ml volumetric flask. Close the flask. The solution is stable for 24 h.

7.3.3 Preparation of the calibration solutions

Introduce into a series of six 250 ml beakers, iron (4.12) and tin standard solutions (4.11.2 and 4.11.3) as indicated in Table 2. Proceed exactly as specified in 7.3.1 and 7.3.2.

Table 2 — Calibration solutions

Addition of tin-free iron g	Volume of tin standard solution (4.11.3) ml	Volume of tin standard solution (4.11.2) ml	Content of tin in final test solution µg
1,0	0	—	0
1,0	1	—	5
1,0	2	—	10
1,0	—	1	50
1,0	—	2	100
1,0	—	5	250
0,5	—	0	0
0,5	—	2	100
0,5	—	2,5	125
0,5	—	3	150
0,5	—	4	200
0,5	—	5	250
0,25	—	0	0
0,25	—	2	100
0,25	—	3	150
0,25	—	4	200
0,25	—	5	250
0,25	—	6	300

7.3.4 Adjustment of the atomic absorption spectrometer

Proceed as specified in Table 3.

Table 3 — Instrumental parameters

Type of lamp	Tin hollow cathode
Wave length	224,6 nm
Flame	Dinitrogen monoxide-acetylene, reducing. The height of the red feather-flame shall be approximately 20 mm adjusted for maximum tin response
Lamp current	Follow manufacturer's recommendations
Band width	Follow manufacturer's recommendations
Background correction	No

7.3.5 Optimization of the atomic absorption spectrometer settings

Follow the manufacturer's instructions for preparation of the instrument for use. When this is done, aspirate 4-methyl-2-pentanone (4.9).

Adjust the instrument to give maximum signal while aspirating the optimization solution (4.13). Continue to aspirate 4-methyl-2-pentanone (4.9) until ready to start measurement.

Evaluate the criteria of 5.1.1 to 5.1.3 and the additional performance requirement of 5.1.4 to ensure that the instrument is suitable for the determination.

7.3.6 Spectrometric measurements

Measure the absorbances, beginning with the lowest calibration solution. Continue with two or three unknown samples, the next lowest calibration solution, two or more unknown samples and so on. In this way, all unknown sample solutions are measured within the same time period as the calibration solutions, excluding any possible drift between calibration and unknown solutions.

8 Plotting the calibration graph

A new calibration graph shall be prepared for each series of determinations.

If pure metals and reagents have been used, the blank test and zero member should give very small absorbance readings with a negligibly small difference. In this case, prepare a calibration graph by plotting the mean absorbance values of the calibration solutions against micrograms of tin in the final test solution.

If, however the zero member has a significant absorbance, a more complicated procedure is required. In this case, the mass of tin m_z in the zero member can be calculated using the formula

$$m_\mathrm{z} = m_1 \times \frac{A_\mathrm{z}}{A_1 - A_\mathrm{z}}$$

where

m_1 is the mass of tin, in micrograms, added to the first calibration solution;

A_z is the absorbance of the zero member;

A_1 is the absorbance of the first calibration solution.

The derived value m_z is then added to each of the nominal calibration masses in order to obtain a mean calibration graph passing through the origin.

9 Expression of results

9.1 Method of calculation

Apply the absorbances of the blank solution (see 7.2) and the test solutions to the calibration graph. Subtract the content of tin in the blank solution from the other results.

The content of tin, expressed as a percentage by mass, w, is given by the equation

$$w = \frac{m_\mathrm{Sn}}{m \times 10^4}$$

where

m_Sn is the content of tin, in micrograms, in the test solution derived from the calibration curve;

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

9.2 Precision

A planned trial of this method was carried out by ten laboratories, at nine levels of tin, each laboratory making three determinations (see notes 1 and 2) of tin at each level.

The test samples used are listed in Table A.1.

The results obtained were treated statistically in accordance with ISO 5725-1, ISO 5725-2 and ISO 5725-3.

The data obtained showed a logarithmic relationship between tin content and repeatability (r) and reproducibility (R_w and R) and test results (see note 3) as summarized in Table 4. The graphical representation of the data is shown in Figure B.1.

Table 4 — Repeatability and reproducibility

Tin content	**Repeatability**	**Reproducibility**	
% by mass	r	R_w	R
0,001	0,000 23	0,000 20	0,000 39
0,003	0,000 42	0,000 42	0,000 77
0,007	0,000 66	0,000 74	0,001 3
0,010	0,000 80	0,000 94	0,001 6
0,020	0,001 2	0,001 5	0,002 5
0,030	0,001 4	0,002 0	0,003 3
0,060	0,002 1	0,003 1	0,005 1
0,090	0,002 6	0,004 1	0,006 5
0,10	0,002 7	0,004 2	0,006 9

NOTE 1 Two of the three determinations were carried out under repeatability conditions as defined in ISO 5725-1, i.e. one operator, same apparatus, identical operating conditions, same calibration and a minimum period of time.

NOTE 2 The third determination was carried out at a different time (on a different day) by the same operator as in note 1 above, using the same apparatus with a new calibration.

NOTE 3 From the results obtained on day 1, the repeatability (r) and the reproducibility (R) were calculated using the procedure specified in ISO 5725-2. From the first result obtained on day 1 and the result obtained on day 2, the within-laboratory reproducibility (R_w), was calculated using the procedure given in ISO 5725-3.

10 Test report

The test report shall include the following information:

a) all information necessary for the identification of the sample, the laboratory and the date of analysis;

b) the method used by reference to this International Standard, i.e. ISO 15353;

c) the results, and the form in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this International Standard or any optional operation which may have influenced the results.

Annex A
(informative)

Additional information on the international co-operative test

Table 4 was derived from the results of international analytical trials carried out from 1994 to 1996 on nine steel samples in six countries involving ten laboratories.

The results of the trials were reported in document ISO/TC 17/SC 1 N 1147. The graphical representation of the precision data is given in annex B.

The test samples used are listed in Table A.1.

Table A.1 — Test samples used

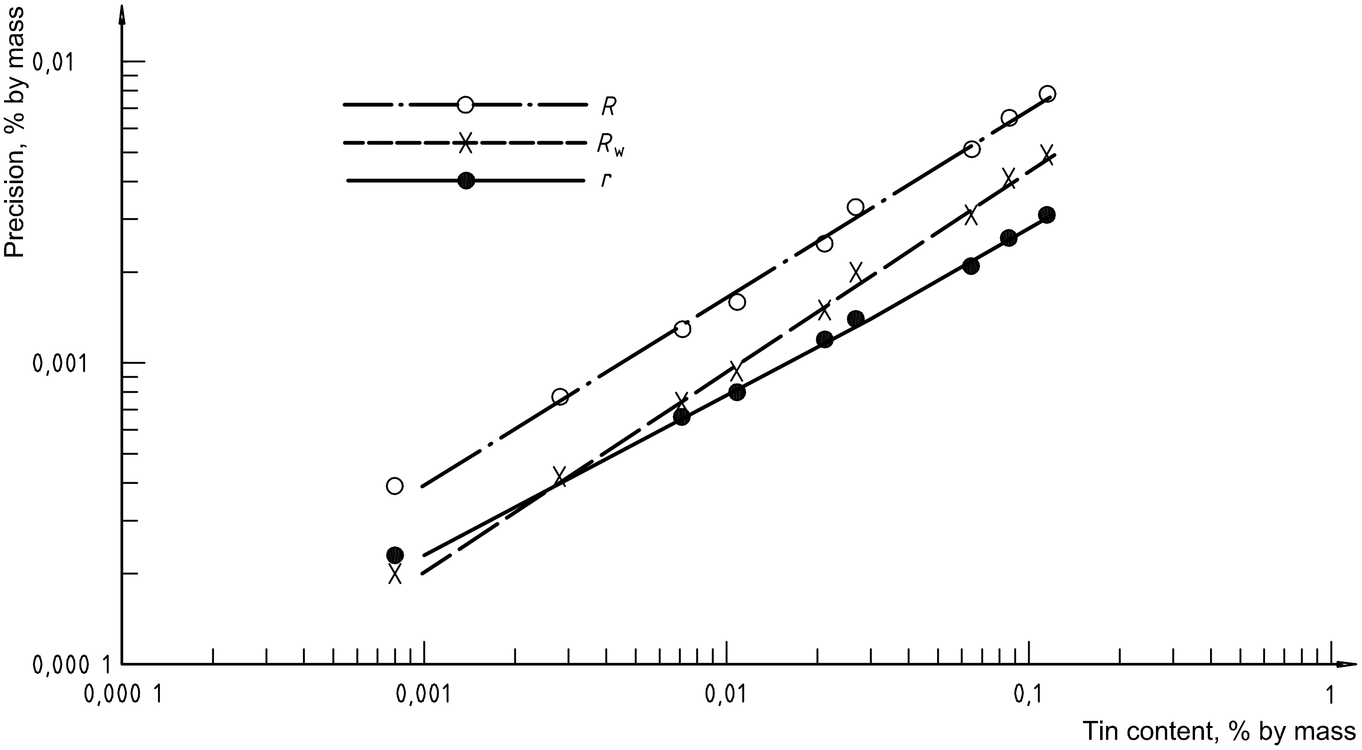
Tin content % by mass				**Precision**		
Sample	**Certified**	**Found**[a]		**Repeatability**	**Reproducibilities**	
		$\overline{w_{\mathrm{Sn1}}}$	$\overline{w_{\mathrm{Sn2}}}$	r	R_{w}	R
NIST 2166 (Low alloy steel)	0,001 0	0,000 8	0,000 80	0,000 23	0,000 20	0,000 39
JK 8F (Stainless steel)	0,002 7	0,002 7	0,002 7	0,000 42	0,000 42	0,000 77
JSS 168-5 (Low alloy steel)	0,007	0,007 1	0,007 1	0,000 66	0,000 74	0,001 3
ECRM 187-1 (Low alloy steel)	0,011	0,010 8	0,010 8	0,000 80	0,000 94	0,001 6
ECRM 185-1 (Alloy steel)	0,021 2	0,021 1	0,021 1	0,001 5	0,001 2	0,002 5
CMSI 1251 (Bearing steel)	0,027 3	0,026 8	0,026 8	0,002 0	0,001 4	0,003 3
A13-Vaskut (Low alloy steel)	0,060	0,064 4	0,063 8	0,002 1	0,003 1	0,005 1
BCS-CRM 455/1 (Carbon steel)	0,085	0,085 7	0,085 4	0,002 6	0,004 1	0,006 5
ECRM 289-1 (High alloy steel)	0,111	0,114 5	0,114 3	0,003 1	0,004 9	0,007 8

[a] $\overline{w_{\mathrm{Sn1}}}$ = general mean within a day

$\overline{w_{\mathrm{Sn2}}}$ = general mean between days

Annex B
(informative)

Graphical representation of precision data



$$\lg r = 0{,}524\,5 \lg \overline{w_{\text{Sn1}}} - 2{,}037\,3$$

$$\lg R_{\text{w}} = 0{,}649\,01 \lg \overline{w_{\text{Sn2}}} - 1{,}723\,9$$

$$\lg R = 0{,}608\,6 \lg \overline{w_{\text{Sn1}}} - 1{,}555$$

Figure B.1 — Graphical representation of precision data

ICS 77.080.01

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