INTERNATIONAL STANDARD

ISO 17058

First edition
2004-02-01

Steel and iron — Determination of arsenic content — Spectrophotometric method

Aciers et fontes — Dosage de l'arsenic — Méthode spectrophotométrique

Reference number
ISO 17058:2004(E)

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Contents

Foreword

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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 17058 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

INTERNATIONAL STANDARD **ISO 17058:2004(E)**

Steel and iron — Determination of arsenic content — Spectrophotometric method

1 Scope

This International Standard specifies a method for the determination of the arsenic content in steel and iron using a spectrophotometric method after distillation.

The method is applicable to an arsenic content between 0,000 5 % (mass fraction) and 0,10 % (mass fraction).

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 385-1:1984, *Laboratory glassware — Burettes — Part 1:General requirements*

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

3 Principle

Dissolution of a test portion in a hydrochloric acid and nitric acid mixture.

Prolonged heating with sulfuric acid until white fumes are given off.

Reduction of arsenic in the presence of hydrazine sulfate and potassium bromide, then separation by distillation as the trivalent chloride, absorbed in the nitric acid solution, in which the As(III) is oxidized back to the pentavalent state As(V).

Formation of the molybdenum blue complex between ammonium molybdate and arsenic which is reduced by hydrazine sulfate.

Spectrophotometric measurement at a wavelength of approximately 840 nm.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only grade 3 water specified in ISO 3696:1987.

4.1 Hydrochloric acid, ρ about 1,19 g/ml

4.2 Nitric acid, ρ about 1,40 g/ml

4.3 Nitric acid, ρ about 1,40 g/ml, diluted 3 + 1

4.4 Acid mixture

Add one volume of nitric acid (4.2) to four volumes of hydrochloric acid (4.1).

4.5 Sulfuric acid, ρ about 1,84 g/ml

4.6 Sulfuric acid, ρ about 1,84 g/ml, diluted 1 + 1

While cooling under water and swirling, add, in small portions, a volume of sulfuric acid (4.5) to an equal volume of water.

4.7 Sulfuric acid, ρ about 1,84 g/ml, diluted 1 + 6

While cooling under water and swirling, add, in small portions, a volume of sulfuric acid (4.5) to six volumes of water.

4.8 Mixture of reducant powder

Weigh, in proportion, 2,5 g of hydrazine sulfate and 10,0 g of potassium bromide, transfer to a mortar and, using a pestle, grind finely and mix well for use.

4.9 Ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 10 g/l

4.10 Hydrazine sulphate, $N_2H_6SO_4$ 0,6 g/l

4.11 Arsenic, standard solution

4.11.1 Stock solution, corresponding to 0,20 g of arsenic per litre

Weigh, to the nearest 0,000 1 g, 0,132 0 g of arsenic trioxide (As_2O_3).

Place in a 100 ml beaker, carefully add 10 ml of nitric acid (4.2), cover with a watch glass, heat gently until dissolution is complete. Add 2 ml of sulphuric acid (4.6), heat cautiously to expel oxides of nitrogen and then evaporate to dense, white fumes.

Remove the beaker from the hot plate, cool somewhat, and wash down the cover and sides of the beaker with a little water.

Again evaporate to copious white fumes.

Remove, cool and add about 10 ml of water, warm gently until salts are dissolved and the solution becomes clear. Cool to room temperature, transfer the solution quantitatively to a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this stock solution contains 0,2 mg of arsenic.

4.11.2 Standard solution A, corresponding to 0,01 g of arsenic per litre

Transfer 25,0 ml of the stock solution (4.11.1) to a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix.

Prepare this solution immediately before use.

1 ml of this standard solution contains 10 µg of arsenic.

4.11.3 Standard solution B, corresponding to 0,002 g of arsenic per litre.

Transfer 50,0 ml of the standard solution (4.11.2) to a 250 ml one-mark volumetric flask. Dilute to the mark with water and mix.

Prepare this solution immediately before use.

1 ml of this standard solution contains 2 µg of arsenic.

4.12 Potassium Bromide

5 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 385-1:1984, ISO 648:1977 and ISO 1042:1998.

Ordinary laboratory apparatus and the following shall be used.

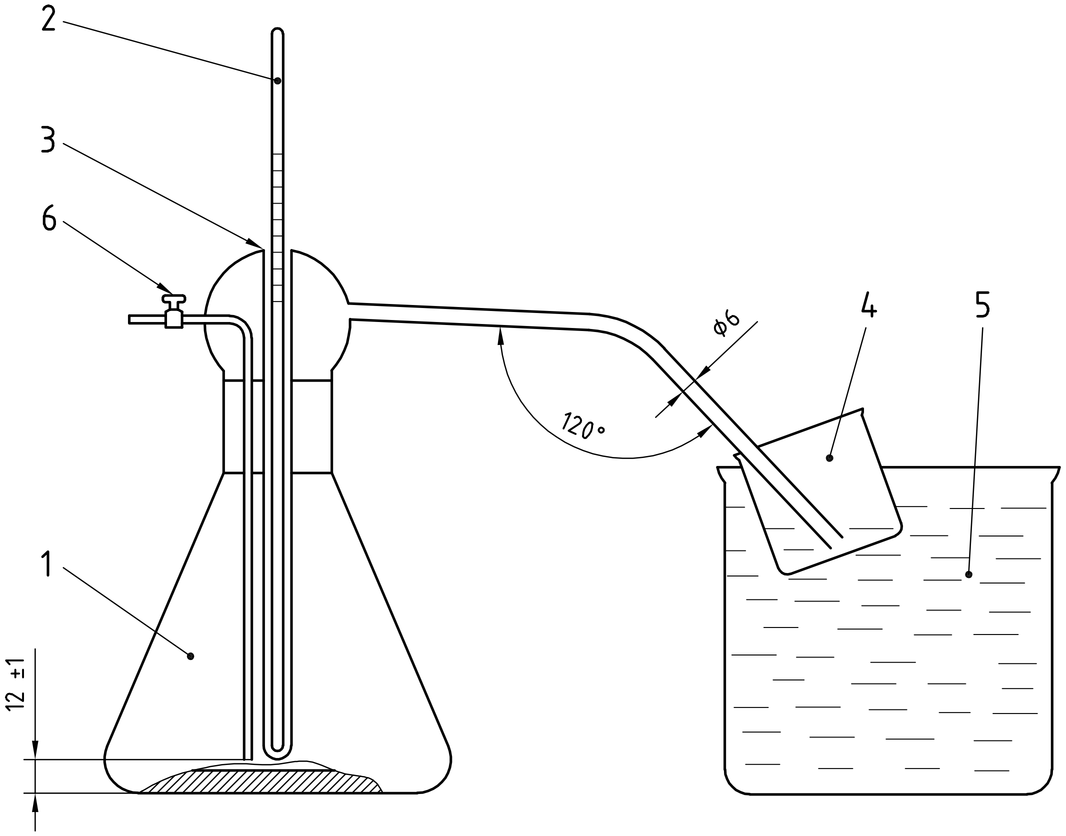
5.1 Spectrophotometer, suitable for measuring the absorbance of the solution at a wavelength of 840 nm with 40 mm (or 10 mm) optical cells

5.2 Distillation apparatus, see attached diagram (Figure 1)

6 Sampling

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

Dimensions in millimetres



Key

1 conical flask (distillation flask), 250 ml
2 thermometer
3 thermometer well
4 receiving beaker, 100 ml
5 cooling beaker, 1 000 ml
6 valve

Figure 1 — Distillation apparatus for arsenic determination

7 Procedure

7.1 Test portion sampling

Weigh, to the nearest 0,1 mg, a test portion of the sample in accordance with Table 1.

Table 1 — Test portion sampling

Expected arsenic content % (mass fraction)	**Test portion** g
0,000 5 to 0,001	1,0
0,001 to 0,006	0,50
0,006 to 0,100	0,10

7.2 Blank test

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

7.3 Determination

7.3.1 Preparation of the test solution

Place the test portion (see 7.1) in a 150 ml beaker. Add 10 ml to 20 ml of the acid mixture (4.4). Cover the beaker with a watch-glass and heat gently to complete dissolution.

Cool the solution, remove the watch-glass and add 20 ml of sulphuric acid (4.6). Replace the watch-glass leaving small opening to allow for the expulsion fumes and evaporate to dense white fumes.

7.3.2 Distillation

Transfer the test solution (see 7.3.1) quantitatively to the distillation flask, rinse down the cover and the sides of the beaker with approximately 10 ml of water. If any undissolved sulfate salts remain, add a small amount of water and warm until the salts are in solution.

Cool in water, add 10 ml of hydrochloric acid (4.1), 2,0 g of mixed reductant powder (4.8), and mix.

Add 10 ml of nitric acid (4.3) to the receiving beaker, and place the beaker in the cooling beaker containing cold water.

Assemble the apparatus for distillation (5.2). Heat the distillation flask at a low temperature, distil until the temperature rises to 125 °C, keeping the entire distillation procedure within 6 min to 10 min. Open the valve to avoid the solution's flowing back from the receiving beaker, and remove the distillation flask from the heat source.

Rinse down the tip of the outlet with a small amount of water. Collect the washings in the receiving beaker. Add 3,5 ml of sulfuric acid (4.7) and mix.

Replace the watch-glass leaving a small opening to allow for the expulsion of fumes and evaporate to dense white sulfuric acid fumes. During this procedure no bubbles should appear.

Remove and cool somewhat, rinse down the cover and the sides of the beaker, and again evaporate to white fumes to expel the oxides of nitrogen.

Remove the beaker from the heat source and allow it to cool. Rinse down the cover and transfer the solution quantitatively to a 50 ml one-mark volumetric flask.

7.3.3 Formation of the coloured complex

Add 2,5 ml of ammonium molybdate solution (4.9) and 2,5 ml of hydrazine sulfate solution (4.10) to the flask, dilute to the mark with water and mix. Warm the flask in a boiling water bath for 10 min. Remove the flask and cool to room temperature.

7.3.4 Spectrophotometric measurements

Carry out spectrophotometric measurements of each solution at a wavelength of about 840 nm after having adjusted the spectrophotometer to zero absorbance by reference to water using 40 mm (or 10 mm) cells.

7.4 Establishment of the calibration graph

7.4.1 Preparation of calibration solution

Introduce into a series of 50 ml one-mark flasks the volumes of arsenic standard solution (4.11.2, 4.11.3) as indicated in Table 2 for arsenic content between 0,000 5 % (mass fraction) and 0,030 % (mass fraction) and Table 3 for arsenic content between 0,030 % (mass fraction) and 0,100 % (mass fraction). Add 2,5 ml of sulfuric acid (4.7) to each one-mark flask.

Proceed as described in 7.3.3.

7.4.2 Spectrophotometric measurements

Carry out spectrophotometric measurements of the range of calibration solutions at a wavelength of about 840 nm after having adjusted the spectrophotometer to zero absorbance by reference to water using 40 mm (or 10 mm) cells.

7.4.3 Plotting the calibration graph

Calculate the difference in absorbance between the solutions and the value obtained for the zero member.

Prepare the straight-line calibration graph, which passes through the origin, by plotting the net absorbance reading against micrograms of arsenic.

Calibration solution for arsenic content between 0, 000 5 % (mass fraction)and 0, 030 % (mass fraction) which 40 mm cells are used shown in Table 2.

Table 2 — Calibration solution for arsenic content between 0, 000 5 % (mass fraction) and 0, 030 % (mass fraction) for which 40 mm cells are used

Volume of arsenic standard solution (4.11.3) ml	**Corresponding mass of arsenic** µg	**Arsenic content of the test sample** % (mass fraction)		
		Test portion of 0,10 g	Test portion of 0,50 g	Test portion of 1,00 g
0 [a]	0	0	0	0
2,0	4			0,000 4
4,0	8	0,008	0,001 6	0,000 8
6,0	12	0,012	0,002 4	
8,0	16	0,016	0,003 2	
10,0	20	0,020	0,004	
15,0	30	0,030	0,006	

[a] Zero member.

Calibration solution for arsenic content between 0, 030 % (mass fraction) and 0, 100 % (mass fraction) which 10 mm cells are used shown in Table 3.

Table 3 — Calibration solution for arsenic content between 0, 030 % (mass fraction) and 0, 100 % (mass fraction) for which 10 mm cells are used

Volume of arsenic standard solution (4.11.2) ml	**Corresponding mass of arsenic** µg	**Arsenic content of the test sample** % (mass fraction) Test portion of 0,10 g
0 [a]	0	0
2,0	20	0,020
4,0	40	0,040
6,0	60	0,060
8,0	80	0,080
10,0	100	0,100

[a] Zero member.

8 Expression of results

8.1 Method of calculation

Convert the absorbance of the test solution and of the blank test solution to micrograms of arsenic by means of the calibration graph (see 7.4).

The arsenic content, W_{As}, expressed as a mass fraction in percent, is given by the equation

$$W_{\mathrm{As}} = \frac{(m_0 - m_1)}{m \times 10^6} \times 100$$

$$= \frac{(m_0 - m_1)}{m \times 10^4}$$

where

m_0 is the mass, expressed in micrograms of arsenic, in the test solution;

m_1 is the mass, expressed in micrograms of arsenic, in the blank value;

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

8.2 Precision

A planned trial of this method was carried out by 8 laboratories, at 9 levels of arsenic, each laboratory making four determinations of arsenic content at each level.

NOTE 1 First two of the four 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 and fourth determinations were carried out at a different time (on a different day), by the same operator as in note 1, using the same apparatus with a new calibration.

The test samples used and mean results obtained are listed in Table A.2.

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 arsenic content and repeatability, r, and reproducibility (R_W and R) of the test results (see Note 3) as summarized in Table 4. The graphical representation of the figures is given in Annex B.

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

Table 4 — Results for repeatability limit and reproducibility limits

Arsenic	**Repeatability limit**	**Reproducibility limits**	
% (mass fraction)	r	R_W	R
0,000 50	0,000 178	0,000 167	0,000 184
0,001 00	0,000 267	0,000 263	0,000 313
0,002 00	0,000 400	0,000 412	0,000 532
0,005 00	0,000 682	0,000 747	0,001 072
0,010 00	0,001 022	0,001 173	0,001 823
0,020 00	0,001 531	0,001 840	0,003 098
0,050 00	0,002 611	0,003 338	0,006 248
0,100 00	0,003 911	0,005 238	0,010 620

9 Test report

The test report shall include the following information:

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

b) the method used by reference to this International Standard;

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 international cooperative tests

The test samples used are listed in Table A.1. Details results for arsenic content obtained in international cooperative tests are shown in Table A.2.

Table A.2 was derived from the results of international analytical trials carried out in 1999 on steel and iron samples in 3 countries involving 8 laboratories.

The results of the trials were reported in document ISO/TC 17/SC 1 N 1272 in 2000. The precision data are presented in graphical form in Annex B.

Table A.1 — Test samples used

No.	Sample	As	C	Si	Mn	Cr	Ni	Others
1	NIST SRM 2167	0,000 5	0,051	0,026	0,022	0,0015	0,002	Cu 0,001 4; Sn 0,006; Sb 0,002 0
2	GSBH41009-93	0,001 0	3,89	1,58	0,65	0,0081	0,0058	Ti 0,042; Sb 0,000 16
3	GSBH40107-96	0,002 2	0,24	0,24	0,49	0,013	0,015	Cu 0,017
4	JSS 169-7	0,005	0,047	0,21	0,42	(0,1)	0,046	Mo 0,068; Ti (0,01); Sn (0,01)
5	BCS461	0,011	0,082	0,44	0,64	15,20	6,16	
6	NIST SRM 50c	0,022	0,719	0,311	0,342	4,13	0,069	V 1,16; W 18,44
7	GBW 01361	0,037	0,318	0,325	0,348	1,93	0,204	Mo 1,19; V 0,301; Sn 0,014; Sb 0,008 6
8	BCS453	0,052	0,210	0,36	—	0,24	0,114	Cu 0,15; Sn 0,019; Ti 0,016, W 0,30
9	BYSC 18201-94	0,092	0,076	1,64	1,10	0,013	0,025	Mo 0,020; Nb 0,012; Sn 0,009 3; Pb 0,003 8

Table A.2 — Detailed results obtained in international cooperative test

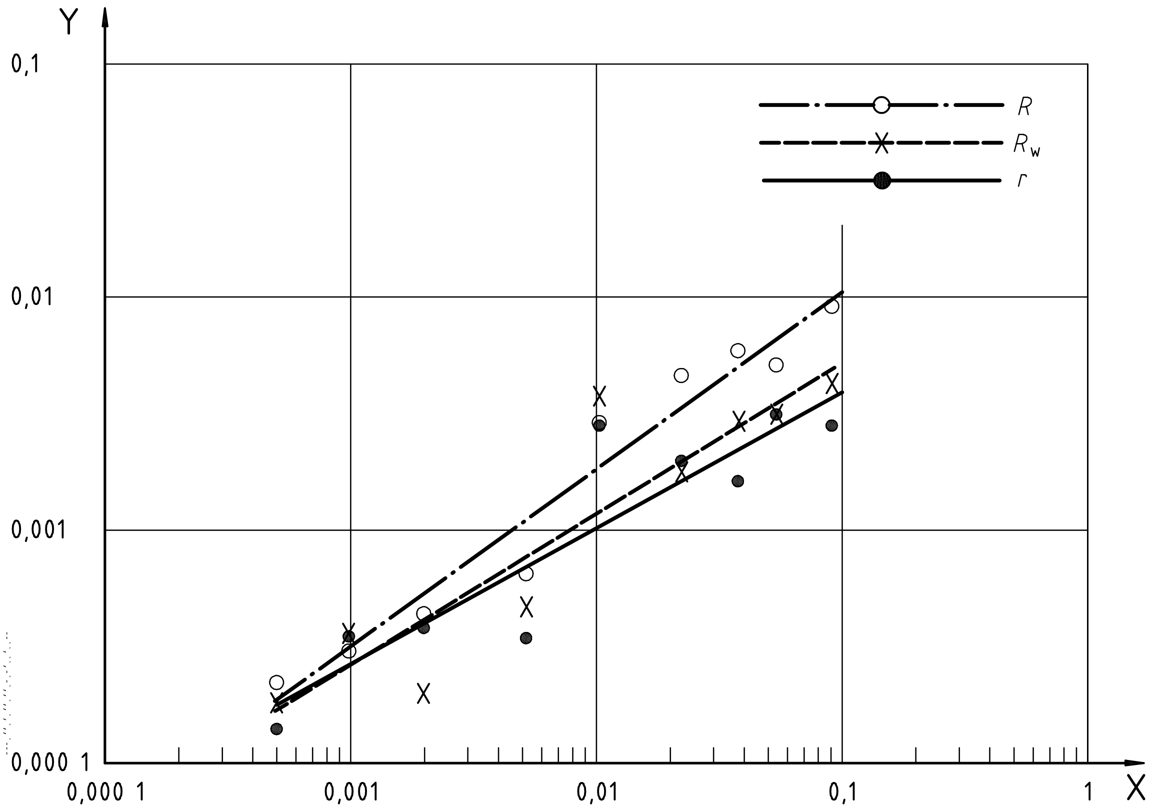
No.	Sample	Arsenic content % (mass fraction)			Precision data		
		Certified	Found $\bar{w}_{\mathrm{As1}}$	Found $\bar{w}_{\mathrm{As2}}$	Repeatability limit r	Reproducibility limits	
						R_{W}	R
1	NIST SRM 2167	0,000 5	0,000 517	0,000 500	0,000 140	0,000 181	0,000 221
2	GSBH41009-93	0,001 0	0,001 000	0,000 985	0,000 349	0,000 360	0,000 302
3	GSBH40107-96	0,002 2	0,001 983	0,001 983	0,000 379	0,000 198	0,000 437
4	JSS 169-7	0,005	0,005 13	0,005 19	0,000 343	0,000 469	0,000 648
5	BCS461	0,011	0,010 0	0,010 3	0,002 800	0,003 757	0,002 892
6	NIST SRM 50c	0,022	0,022 3	0,022 2	0,001 980	0,001 771	0,004 606
7	GBW 01361	0,037	0,037 4	0,037 75	0,001 617	0,002 914	0,005 879
8	BCS453	0,052	0,054 0	0,053 9	0,003 130	0,003 130	0,005 099
9	BYSC 18201-94	0,092	0,090 7	0,090 9	0,002 800	0,004 246	0,009 116

$\bar{w}_{\mathrm{As1}}$: general mean within a day

$\bar{w}_{\mathrm{As2}}$: general mean over several days

Annex B
(informative)

Graphical representation of precision data



Key

X Arsenic content, mass fraction %

Y Precision, mass fraction %

$\log r = 0{,}582\,9 \log w_{\mathrm{As1}} - 1{,}824\,8$

$\log R_{\mathrm{w}} = 0{,}65 \log w_{\mathrm{As2}} - 1{,}630\,8$

$\log R = 0{,}765\,4 \log w_{\mathrm{As1}} - 1{,}208\,4$

Figure B.1 — Logarithmic relationship between arsenic content ($\overline{w}_{\mathrm{As1}}$ or $\overline{w}_{\mathrm{As2}}$), repeatability limit, r, and reproducibility limits, R_{W} and R

Bibliography

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

[2] ISO 5725-2, *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*

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

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