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Low-alloyed steel — Determination of Mn, P, Cr, Ni, Mo, Co, Cu, V, Ti, As and Sn — Inductively coupled plasma optical emission spectrometric method

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Low-alloyed steel — Determination of Mn, P, Cr, Ni, Mo, Co, Cu, V, Ti, As and Sn — Inductively coupled plasma optical emission spectrometric method

1 Scope

This document specifies a method for the determination of Mn, P, Cr, Ni, Mo, Co, Cu, V, Ti, As and Sn contents in low alloyed steel by inductively coupled plasma optical emission spectrometry (ICP-OES).

The method is applicable to the determination of Mn, P, Cr, Ni, Mo, Co, Cu, V, Ti, As and Sn within the ranges given in Table 1.

Table 1 — Application ranges of the elements to be determined

Element	Application range % (mass fraction)
Mn	0,002 to 2,0
P	0,005 to 0,1
Cr	0,003 to 3,0
Ni	0,005 to 4,0
Mo	0,003 to 1,0
Co	0,002 to 0,2
Cu	0,003 to 0,5
V	0,002 to 0,5
Ti	0,002 to 0,5
As	0,003 to 0,1
Sn	0,003 to 0,08

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 — Single-volume pipettes*

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

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

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

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

Dissolution of a test portion in nitric and hydrochloric acids. Filtration and ignition of the acid insoluble residue. Removal of silica with hydrofluoric acid.

Fusion of the residue with potassium hydrogen sulfate, dissolution of the melt with acid and addition of this solution to the reserved filtrate. If necessary, addition of an internal standard element and dilution of the solution to a known volume.

Nebulization of the solution into an ICP-OES spectrometer and measurement of the intensity of the emitted light from each element simultaneously with the intensity of the light emitted by the internal standard element.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only grade 2 water as specified in ISO 3696.

5.1 Pure iron, containing at least ten times less than the lower limit of the scope of each element to be determined.

5.2 Potassium hydrogen sulfate ($KHSO_4$) or potassium disulfate ($K_2S_2O_7$).

5.3 Hydrochloric acid, ρ about 1,19 g/ml.

5.4 Nitric acid, ρ about 1,42 g/ml.

5.5 Nitric acid solution, ρ about 1,42 g/ml, diluted 1 + 1.

5.6 Hydrofluoric acid, ρ about 1,15 g/ml.

5.7 Sulfuric acid, ρ about 1,84 g/ml.

5.8 Sulfuric acid solution, ρ about 1,84 g/ml, diluted 1 + 3.

5.9 Manganese standard solution, 1 g/l.

Transfer several grams of electrolytic manganese (purity > 99,9 %) into a 250 ml beaker containing about 150 ml of sulphuric acid solution (ρ about 1,84 g/ml, diluted 5+95). Stir, then allow the manganese to settle for several minutes. Decant and eliminate the sulphuric acid solution and substituting water. Wash several times with water and finally with acetone. Dry the metal for about 2 min at 100 °C and cool in a desiccator.

Weigh, to the nearest 1 mg, 1,000 g of manganese as mentioned above. Transfer into a 250 ml beaker, add 40 ml of hydrochloric acid (5.3) and cover with a watch-glass. Heat gently to complete dissolution. Cool, transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 1 mg of manganese.

5.10 Phosphorus standard solution, 1 g/l.

Weigh, to the nearest 0,1 mg, 4,393 6 g of potassium dihydrogen phosphate (KH_2PO_4) previously dried to constant mass at 110 °C and cooled in a desiccator.

Transfer into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 1 mg of phosphorus.

5.11 **Chromium standard solution,** 1 g/l.

Prepare a 1 g/l chromium standard solution by using one of the procedures described in a) or b).

a) Weigh, to the nearest 1 mg, 1,000 g of chromium [purity ≥ 99,9 % (mass fraction)]. Transfer into a 250 ml beaker, add 40 ml of hydrochloric acid (5.3) and cover with a watch-glass. Heat gently to complete dissolution. Cool, transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

b) Weigh 2,828 4 g of potassium dichromate ($K_2Cr_2O_7$), previously dried at 140 °C and allowed to cool in a desiccator. Place in a 400 ml beaker and dissolve in about 20 ml of water. Add 5 ml of the sulfuric acid (5.7) and, while cooling, cautiously add the hydrogen peroxide solution (to be added), adding an excess of about 2 ml after effervescence has ceased. Allow the solution to stand at ambient temperature until the yellow colour has completely disappeared (several hours), then transfer into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this standard solution contains 1 mg of chromium.

5.12 **Nickel standard solution,** 1 g /l.

Weigh, to the nearest 1 mg, 1,000 g of nickel [purity ≥ 99,9 % (mass fraction)]. Transfer into a 250 ml beaker, add 50 ml of nitric acid (5.5) and cover with a watch-glass. Heat gently to complete dissolution. Cool, transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 1 mg of nickel.

5.13 **Molybdenum standard solution,** 1 g /l.

Weigh, to the nearest 1 mg, 1,000 g of molybdenum [purity ≥ 99,9 % (mass fraction)]. Transfer into a 250 ml beaker, add 50 ml of hydrochloric acid (5.3) and 50 ml of nitric acid (5.4) and cover with a watch-glass. Heat gently to complete dissolution. Cool, transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 1 mg of molybdenum.

5.14 **Cobalt standard solution,** 1 g/l.

Weigh, to the nearest 1 mg, 1,000 g of cobalt [purity ≥ 99,9 % (mass fraction)]. Transfer into a 250 ml beaker, add 50 ml of nitric acid solution (5.5) and cover with a watch-glass. Heat gently to complete dissolution. Cool, transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 1 mg of cobalt.

5.15 **Copper standard solution,** 1 g/l.

Weigh, to the nearest 1 mg, 1,000 g of copper [purity ≥ 99,9 % (mass fraction)]. Transfer into a 250 ml beaker, add 50 ml of nitric acid solution (5.5) and cover with a watch-glass. Heat gently to complete dissolution. Cool, transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 1 mg of copper.

5.16 Vanadium standard solution, 1 g/l.

Weigh, to the nearest 1 mg, 1,000 g of vanadium [purity ≥ 99,9 % (mass fraction)]. Transfer into a 250 ml beaker, add 30 ml of aqua regia [mix three volume of hydrochloric acid (5.3) with one volume of nitric acid (5.4)] and cover with a watch-glass. Heat gently to complete dissolution. Cool, transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 1 mg of vanadium.

5.17 Titanium standard solution, 1 g/l.

Weigh, to the nearest 1 mg, 200 mg of titanium [purity ≥ 99,9 % (mass fraction)]. Transfer into a 250 ml beaker, add 50 ml of hydrochloric acid (5.3), diluted 1 + 1 and 5 drops of hydrofluoric acid (5.6) and cover with a watch-glass. Heat gently to complete dissolution. Cool, transfer the solution quantitatively into to a 200 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 1 mg of titanium.

5.18 Arsenic standard solution, 100 mg/l.

Prepare an arsenic standard solution by using one of the procedures described in a) or b).

a) Weigh, to the nearest 1 mg, 100 mg of arsenic [purity ≥ 99,9 % (mass fraction)]. Transfer into a 250 ml beaker, add 20 ml of nitric acid solution (5.5) and cover with a watch-glass. Heat gently to complete dissolution. Cool, transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

b) Weigh, to the nearest 1 mg, 132 mg of arsenic trioxide. Transfer into a 250 ml beaker, add 6 ml of potassium hydroxide solution (10 g/l) and dilute with water to 100 ml. Adjust the pH between 3 and 6 with hydrochloric acid (diluted 1+10). Transfer the solution quantitatively into 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 0,1 mg of arsenic.

5.19 Tin standard solution, 500 mg/l.

Weigh, to the nearest 1 mg, 500 mg of tin [purity ≥ 99,9 % (mass fraction)]. Transfer into a 250 ml beaker, add 20 ml of hydrochloric acid (5.3) and 5 ml of nitric acid (5.4) and cover with a watch-glass. Heat gently to complete dissolution. Remove from the hot plate immediately and allow to cool. Transfer the solution into a 1 000 ml one-mark volumetric flask containing 200 ml of hydrochloric acid (5.3). Dilute to the mark with water and mix.

1 ml of this standard solution contains 0,5 mg of tin.

5.20 Yttrium internal standard solution, 100 mg/l.

Calcine several grams of yttrium oxide [purity ≥ 99,9 % (mass fraction)] in a muffle furnace at 850 °C ± 10 °C for at least 40 min and then allow to cool in a desiccator. Weigh 0,127 0 g of the calcined product, transfer into a 250 ml beaker, add 10 ml of hydrochloric acid (5.3) and cover with a watch-glass. Heat gently to complete dissolution. Cool, transfer the solution into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 0,1 mg of yttrium.

NOTE Elements as cadmium and scandium can also be used as internal standards.

5.21 Multi-elemental standard solutions for Mn, P, Cr, V and Ti

5.21.1 Multi-elemental standard solution for Mn, P, Cr, V and Ti, corresponding to 100 mg of each element per litre.

Transfer 10,0 ml of each of the standard solutions (5.9), (5.10), (5.11), (5.16) and (5.17) into a 100 ml one-mark volumetric flask. Add 5 ml hydrochloric acid (5.3), dilute to the mark with water and mix.

1 ml of this standard solution contains 100 µg of Mn, P, Cr, V and Ti.

5.21.2 Multi-elemental standard solution for Mn, P, Cr, V and Ti, corresponding to 10 mg of each element per litre.

Transfer 10,0 ml of the multi-elemental standard solution (5.21.1) into a 100 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 10,0 µg of Mn, P, Cr, V and Ti.

Prepare this solution immediately before use.

5.22 Multi-elemental standard solutions for Ni, Mo, Co, Cu, As and Sn.

5.22.1 Multi-elemental standard solution for Ni, Mo, Co, Cu and Sn, corresponding to 100 mg of each element per litre.

Transfer 10,0 ml of each of the standard solutions (5.12), (5.13), (5.14) and (5.15) and 20,0 ml of tin standard solution (5.19) into a 100 ml one-mark volumetric flask. Add 5 ml hydrochloric acid (5.3), dilute to the mark with water and mix.

1 ml of this standard solution contains 100 µg of Ni, Mo, Co, Cu and Sn.

5.22.2 Multi-elemental standard solution for Ni, Mo, Co, Cu, As and Sn, corresponding to 10 mg of each element per litre.

Transfer 10,0 ml of the multi-elemental standard solution (5.22.1) and 10,0 ml of arsenic standard solution (5.18) into a 100 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 10,0 µg of Ni, Mo, Co, Cu, As and Sn.

Prepare this solution immediately before use.

NOTE Standard solutions whose preparations are described under items 5.9 to 5.20 can be replaced by commercially available standard solutions, provided that they are supplied by a recognised producer and their traceability fully documented.

6 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 648 or ISO 1042 as appropriate.

Ordinary laboratory apparatus and the following shall be used.

6.1 Optical emission spectrometer, equipped with an inductively coupled plasma (ICP-OES).

The ICP-OES used will be satisfactory if, after optimizing according to 8.4, it meets the performance criteria given in 6.1.2 to 6.1.5.

The spectrometer can be either simultaneous or sequential. If a sequential spectrometer can be equipped with an extra arrangement for simultaneous measurement of the internal standard wavelength, it can be used with the internal standard technique. If the sequential spectrometer is not equipped with this arrangement, the internal standard cannot be used and an alternative technique without internal standard shall be applied.

6.1.1 Wavelengths

This method does not specify any particular emission line. It is mandatory that each laboratory carefully investigate the wavelengths available on its own equipment to find the most suitable one regarding sensitivity and absence of interferences.

In Table 2, however, several suggestions are given together with possible interferences. These wavelengths have been carefully investigated.

The wavelength of the internal standard element chosen shall not interfere with the analytical wavelengths, nor should the internal element wavelength be interfered by elements present in the test solution. It is, however, recommended to use Y 371,030 nm. This wavelength is free of interferences from the elements.

Table 2 — Wavelengths and interfering elements

Element	Wavelength nm	Possible interferences
Mn	257,610	—
	260,569	Co, Fe, Cr
P	178,280	Mo, Cr, Mn
	213,618	Mo, Cu
Cr	267,716	Mn
	206,149	—
Ni	231,604	Co
	221,647	—
Mo	202,030	Fe
	281,615	Al, V
Co	228,616[a]	Cr, Ti, Ni
Cu	324,754	Mn, Mo
	327,396	Mo
V	309,311	Fe
	311,071	Ti, Mo
Ti	334,941	Cr
	337,280	—
As	189,042	Cr
	193,759	—
Sn	189,989	—
	283,999	Cr
Y	371,030	None

[a] Check and correct, if necessary, for interference by Ni and Cr

Other element can be used as internal standard, but it shall not be present in the sample and interfere with the analytical wavelengths, nor shall elements present in the test solution interfere with the internal element wavelength. Moreover, the excitation conditions of the analytical lines and the internal standard element line should match.

6.1.2 Minimum practical resolution of the spectrometer

Calculate the bandwidth, according to A.1, for the wavelength used including the wavelength of the internal standard. The bandwidth shall be less than 0,030 nm.

6.1.3 Minimum short-term precision

Calculate the short-term precision according to A.2. The relative standard deviation (RSD) shall not exceed 0,5 % for concentrations 100 to 1 000 times above the LOD (6.1.5). For concentrations 10 to 100 times above the LOD (6.1.5), the RSD shall not exceed 5 %.

6.1.4 Long-term stability

Calculate the standard deviation of seven mean values of three measurements of the absolute intensity or intensity ratio of the emitted light of the most concentrated calibration solution for each element. Each mean value should be determined every 30 min during a total time of 3 h. The relative standard deviation shall not exceed 2 % for the absolute intensity technique or 1,5 % for the internal standard technique.

6.1.5 Limit of detection (LOD) and limit of quantification (LOQ)

Calculate the LOD and LOQ, according to the A.3, for the wavelength used. The values shall be below the values in Table 3.

Table 3 — Limit of detection (LOD) and limit of quantification (LOQ)

Element	Wavelength nm	LOD mg/l	LOQ mg/l
Mn	257,610	0,03	0,1
	260,569	0,03	0,1
P	178,280	0,06	0,2
	213,618	0,06	0,2
Cr	267,716	0,03	0,1
	206,149	0,03	0,1
Ni	231,604	0,06	0,2
	221,647	0,06	0,2
Mo	202,030	0,03	0,1
	281,615	0,03	0,1
Co	228,616	0,03	0,1
Cu	324,754	0,03	0,1
	327,396	0,03	0,1
V	309,311	0,03	0,1
	311,071	0,03	0,1
Ti	334,941	0,03	0,1
	337,280	0,03	0,1
As	189,042	0,03	0,1
	193,759	0,03	0,1
Sn	189,989	0,03	0,1
	283,999	0,03	0,1

6.1.6 Linearity of the calibration curves

The linearity of the calibration curves is checked by calculating the correlation coefficient. This coefficient shall be higher than 0,999.

6.2 Platinum crucible, of capacity 30 ml.

7 Sampling and sample preparation

Sampling and sample preparation shall be carried out in accordance with ISO 14284 or with an appropriate national standard for steels.

8 Procedure

8.1 Test portion

Weigh, to the nearest 0,001 g, 0,500 g of the test sample.

8.2 Blank test

In parallel with the determination of the content and following the same procedure, carry out a blank test using the same quantities of all the reagents, including pure iron (5.1).

8.3 Determination

8.3.1 Preparation of the test solution

8.3.1.1 Dissolution of the test portion

Transfer the test portion (see 8.1) into a 250 ml beaker. Add 10 ml of nitric acid solution (5.5), cover the beaker with a watch-glass and heat gently until the acid action ceases and then boil for 1 min. Add 5 ml of hydrochloric acid (5.3) and continue the heating to boil for about 5 min.

Allow to cool, add about 15 ml of water, filter through a close texture filter paper and collect the filtrate in a 100 ml one-mark volumetric flask. Wash the filter paper several times with hot water and collect the washings in the volumetric flask. Reserve the filtrate as the main solution. Check the filter paper carefully for residue. If there is no residue, skip the procedure described in 8.3.1.2.

8.3.1.2 Treatment of insoluble residue

Transfer the filter paper and residue into a platinum crucible (6.2), dry and ignite at a temperature as low as possible until all carbonaceous matter is removed and finally at about 800 °C for at least 15 min. Cool, add 2 drops of sulfuric acid solution (5.8) and about 2 ml of hydrofluoric acid (5.6). Evaporate to dryness, heat to about 800 °C and cool. Add 1 g of potassium hydrogen sulfate (5.2) and fuse carefully until a clear melt is obtained.

For residues containing carbides, prolonged heating may be necessary for complete fusion. The potassium hydrogen sulfate can be regenerated by allowing the melt to cool, adding 2 drops of sulfuric acid (5.7) and repeating the fusion until the residue is dissolved.

After cooling, add 10 ml of water and 2 ml of hydrochloric acid (5.3) to the solidified melt in the crucible, transfer the contents to a 250 ml beaker and heat gently until the fusion products are dissolved. Cool and add this solution to the main solution (see 8.3.1.1).

8.3.1.3 Dilution of the test solution

If the internal standard technique is used, add 5,0 ml of the yttrium internal standard solution (5.20) (see NOTE). Dilute to the mark with water and mix.

NOTE Elements as cadmium and scandium can also be used as internal standard.

8.3.2 Preparation of the calibration solutions

Transfer 0,48 g ± 0,005 g of pure iron (5.1) into each of a series of nine 250 ml beakers. Treat the pure iron following the same procedure as the test portion (see 8.3.1.1). Procedure 8.3.1.2 is not necessary, provided that the same amount of all the appropriate reagents are added. If the procedure 8.3.1.2 is skipped in preparation of the test solutions, just follow the procedure of 8.3.1.1 to treat the pure iron.

Transfer the solution into each of a series of nine 100 ml one-mark volumetric flasks, rinsing the beakers with a minimum quantity of water.

Add to the volumetric flasks the volumes of the standard solutions (see NOTE 1 and NOTE 2) given in Table 4. Corresponding contents in the test portion are listed in Table 5. If the internal standard technique is used, add 5,0 ml of yttrium internal standard solution (5.20) (see NOTE 3). Dilute to the mark with water and mix.

NOTE 1 The whole elements can also be added one by one to the calibration solutions if multi-elemental solutions are not prepared.

NOTE 2 Calibration curves can be adapted according to the content range of test samples, but the calibration solutions shall not be less than 5.

NOTE 3 Cadmium and scandium can also be used as internal standard.

Table 4 — Standard solutions volumes (ml)

Calibration solution No.	Multi-elemental standard solution (5.21)	Manganese standard solution (5.9)	Chromium standard solution (5.11)	Multi-elemental standard solution (5.22)	Nickel standard solution (5.12)	Molybdenum standard solution (5.13)	Arsenic standard solution (5.18)
$S_0$1)	0	0	0	0	0	0	0
S_1	1,00 (5.21.2)	0	0	0	20,00	0	0
S_2	2,50 (5.21.2)	0	0	0	10,00	0	0
S_3	5,00 (5.21.2)	0	0	0	5,00	5,00	0
S_4	2,50 (5.21.1)	0	0	25,00 (5.22.1)	0	0	0
S_5	5,00 (5.21.1)	0	0	5,00 (5.22.1)	0	0	5,00
S_6	25,00 (5.21.1)	0	0	2,50 (5.22.1)	0	0	2,50
S_7	0	5,00	5,00	5,00 (5.22.2)	0	0	0
S_8	0	10,00	10,00	2,50 (5.22.2)	0	0	0
S_9	0	0	15,00	1,00 (5.22.2)	0	0	0

1) Zero member

Table 5 — Corresponding content of each element in the test portion % (mass fraction)

Calibration solution No.	Mn	P	Cr	V	Ti	Ni	Mo	Co	Cu	As	Sn
$S_0$1)	0	0	0	0	0	0	0	0	0	0	0
S_1	0,002	0,002	0,002	0,002	0,002	4,00	---	---	---	---	---
S_2	0,005	0,005	0,005	0,005	0,005	2,00	---	---	---	---	---
S_3	0,010	0,010	0,010	0,010	0,010	1,00	1,00	---	---	---	---
S_4	0,050	0,050	0,050	0,050	0,050	0,50	0,50	0,50	0,50	---	0,50
S_5	0,10	0,10	0,10	0,10	0,10	0,10	0,10	0,10	0,10	0,10	0,10
S_6	0,50	0,50	0,50	0,50	0,50	0,050	0,050	0,050	0,050	0,050	0,050
S_7	1,00	---	1,00	---	---	0,010	0,010	0,010	0,010	0,010	0,010
S_8	2,00	---	2,00	---	---	0,005	0,005	0,005	0,005	0,005	0,005
S_9	----	---	3,00	---	---	0,002	0,002	0,002	0,002	0,002	0,002

1) Zero member

8.4 Preparation for spectrometric measurements

Start the ICP-OES and let it stabilize in accordance to the manufacturer's instructions before any measurement.

Optimize the instrument according to the manufacturer's instructions.

Prepare the software to measure the intensity, and for the calculation of the mean value and relative standard deviation corresponding to each wavelength.

If an internal standard is used, prepare the software to calculate the ratio between the analyte intensity and the internal standard intensity. The intensity of the internal standard shall be measured simultaneously with the analyte intensity.

Check the instrument performance requirements given in 6.1.2 to 6.1.5.

8.5 Measurement of the calibration solutions

Measure the absolute intensities or the ratioed intensities of the analytical lines beginning with the calibration solution S_0 and ending up with the calibration solution S_9.

Measure each of the calibration solution three times and calculate the mean intensities.

Subtract the mean absolute intensity or the mean ratioed intensity (I_{c0}) of the calibration solution S_0 (zero member) from the mean absolute intensity or the mean ratioed intensity (I_{ci}) of each solution in order to obtain the net absolute intensity or the net ratioed intensity (I_{cN}).

8.6 Calibration curves

Calculate the linear regression functions through the points representing the intensities or the ratioed intensities of each element on the y-axis and the corresponding concentration, ρ_i, expressed in micrograms per millilitre, of the calibration solutions on the x-axis.

Calculate the correlation coefficient of each curve. The coefficients shall meet the specification given in 6.1.6.

NOTE The accuracy can be improved by splitting the calibration curves, especially for the elements with wide content ranges, such as manganese, chromium and nickel. The boundary point can be set as 0,1 %, i.e., the calibration curve of manganese can be divided into two parts: one part is from 0 to 0,1 % and another part is from 0,1 % to 2,0 %.

8.7 Measurements of the test solution

Measure the absolute intensity or ratioed intensity of each test solution three times and calculate the mean intensities.

Subtract the mean absolute intensity or the mean ratioed intensity (I_0) of the blank test (zero member) from the mean absolute intensity or the mean ratioed intensity (I_i) of each test solution giving the net absolute intensity or the net ratioed intensity (I_N).

9 Expression of results

9.1 Method of calculation

Using the linear regression functions calculated in 8.6 and the net absolute intensity, or the net ratioed intensity of the test solution measured in 8.7, calculate the concentration of each element in the test solution, expressed in micrograms per millilitre.

NOTE Most of the ICP-OES software can calculate the concentration of each element in the test solution automatically.

The content of the element, w_i, expressed as a percentage by mass, is given by the Formula (1):

$$w_i = \frac{\rho_i \times 100 \times 10^{-6}}{m} \times 100 \qquad (1)$$

where

ρ_i is the concentration, expressed in microgram per millilitre, of the element, *i*, in the test solution;

m is the mass of the test portion, expressed in gram.

9.2 Precision

A planned trial of this method was carried out by 11 laboratories, at 5 levels to 10 levels of each element, each laboratory making three determinations for each element at each level.

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, using the same apparatus with a new calibration.

The test samples used are listed in Annex B. The results obtained were treated statistically in accordance with ISO 5725-2 and ISO 5725-3.

The relationship between the content of each element and repeatability limit (r) and reproducibility limits (R_w and R) of the test results (see NOTE 3) is summarized in Table 6 to Table 16. The graphical representations of the data are shown in Annex C.

NOTE 3 From the two values obtained on day 1 and the value obtained on day 2, the repeatability limit (r) and reproducibility limit (R_w and R) were calculated using the procedure specified in ISO 5725-3.

Table 6 — Manganese — Precision data (smoothed values)

Manganese % (mass fraction)	**Repeatability limit** ***r*** % (mass fraction)	**Reproducibility limits** R_w % (mass fraction)	 ***R*** % (mass fraction)
0,002	0,000 4	0,000 5	0,001 2
0,005	0,000 7	0,000 9	0,001 9
0,01	0,001 1	0,001 4	0,002 8
0,02	0,001 6	0,002 1	0,004 1
0,05	0,002 8	0,003 6	0,006 8
0,1	0,004	0,005	0,010
0,2	0,006	0,008	0,015
0,5	0,010	0,014	0,024
1	0,015	0,021	0,036
2	0,023	0,032	0,052

Table 7 — Phosphorus — Precision data (smoothed values)

Phosphorus	**Repeatability limit**	**Reproducibility limits**	
% (mass fraction)	***r*** % (mass fraction)	R_w % (mass fraction)	***R*** % (mass fraction)
0,005	0,000 5	0,000 7	0,001 2
0,01	0,000 7	0,001 0	0,001 8
0,02	0,001 0	0,001 3	0,002 7
0,05	0,001 5	0,002 0	0,004 5
0,1	0,002 1	0,002 8	0,006 7

Table 8 — Chromium — Precision data (smoothed values)

Chromium	**Repeatability limit**	**Reproducibility limits**	
% (mass fraction)	***r*** % (mass fraction)	R_w % (mass fraction)	***R*** % (mass fraction)
0,003	0,000 5	0,001 1	0,001 5
0,005	0,000 5	0,001 1	0,001 6
0,01	0,000 6	0,001 2	0,001 8
0,02	0,000 8	0,001 5	0,002 1
0,05	0,001 3	0,002 2	0,003 2
0,1	0,002	0,003	0,005
0,2	0,004	0,006	0,008
0,5	0,009	0,013	0,019
1	0,017	0,025	0,037
2	0,034	0,049	0,072
3	0,050	0,073	0,107

Table 9 — Nickel — Precision data (smoothed values)

Nickel	**Repeatability limit**	**Reproducibility limits**	
% (mass fraction)	***r*** % (mass fraction)	R_w % (mass fraction)	***R*** % (mass fraction)
0,005	0,000 6	0,000 6	0,001 6
0,01	0,000 9	0,001 0	0,002 5
0,02	0,001 5	0,001 7	0,003 8
0,05	0,002 6	0,003 3	0,006 8
0,1	0,004	0,006	0,011
0,2	0,006	0,009	0,016
0,5	0,011	0,019	0,029
1	0,017	0,031	0,046
2	0,026	0,053	0,071
4	0,040	0,089	0,110

Table 10 — Molybdenum — Precision data (smoothed values)

Molybdenum % (mass fraction)	**Repeatability limit**	**Reproducibility limits**	
	r % (mass fraction)	R_w % (mass fraction)	***R*** % (mass fraction)
0,003	0,000 4	0,000 5	0,001 1
0,005	0,000 5	0,000 6	0,001 4
0,01	0,000 8	0,001 0	0,002 1
0,02	0,001 2	0,001 5	0,003 1
0,05	0,002 1	0,002 8	0,005 2
0,1	0,003	0,004	0,008
0,2	0,005	0,007	0,011
0,5	0,009	0,012	0,019
1	0,013	0,019	0,028

Table 11 — Cobalt — Precision data (smoothed values)

Cobalt % (mass fraction)	**Repeatability limit**	**Reproducibility limits**	
	r % (mass fraction)	R_w % (mass fraction)	***R*** % (mass fraction)
0,002	0,000 3	0,000 5	0,001 0
0,005	0,000 4	0,000 6	0,001 2
0,01	0,000 5	0,000 7	0,001 5
0,02	0,000 6	0,001 0	0,002 1
0,05	0,001 1	0,002 0	0,004 0
0,1	0,002	0,004	0,007
0,2	0,004	0,007	0,013

Table 12 — Copper — Precision data (smoothed values)

Copper % (mass fraction)	**Repeatability limit**	**Reproducibility limits**	
	r % (mass fraction)	R_w % (mass fraction)	***R*** % (mass fraction)
0,003	0,000 5	0,000 6	0,001 5
0,005	0,000 5	0,000 7	0,001 6
0,01	0,000 6	0,000 9	0,001 9
0,02	0,000 9	0,001 3	0,002 4
0,05	0,001 6	0,002 4	0,004 1
0,1	0,003	0,004	0,007
0,2	0,005	0,008	0,013
0,5	0,012	0,020	0,030

Table 13 — Vanadium — Precision data (smoothed values)

Vanadium % (mass fraction)	Repeatability limit r % (mass fraction)	Reproducibility limits R_w % (mass fraction)	 R % (mass fraction)
0,002	0,000 1	0,000 3	0,000 8
0,005	0,000 3	0,000 6	0,001 5
0,01	0,000 4	0,000 9	0,002 3
0,02	0,000 7	0,001 4	0,003 5
0,05	0,001 5	0,002 5	0,006 2
0,1	0,002	0,004	0,009
0,2	0,004	0,006	0,015
0,5	0,008	0,012	0,026

Table 14 — Titanium — Precision data (smoothed values)

Titanium % (mass fraction)	Repeatability limit r % (mass fraction)	Reproducibility limits R_w % (mass fraction)	 R % (mass fraction)
0,002	0,000 2	0,000 3	0,000 4
0,005	0,000 3	0,000 5	0,000 8
0,01	0,000 4	0,000 9	0,001 3
0,02	0,000 7	0,001 5	0,002 3
0,05	0,001 3	0,003 0	0,004 6
0,1	0,002	0,005	0,008
0,2	0,003	0,008	0,014
0,5	0,006	0,017	0,028

Table 15 — Arsenic — Precision data (smoothed values)

Arsenic % (mass fraction)	Repeatability limit r % (mass fraction)	Reproducibility limits R_w % (mass fraction)	 R % (mass fraction)
0,003	0,000 4	0,000 9	0,001 3
0,005	0,000 5	0,001 0	0,001 6
0,01	0,000 7	0,001 3	0,002 3
0,02	0,001 0	0,001 6	0,003 3
0,05	0,001 4	0,002 2	0,005 2
0,1	0,001 8	0,002 8	0,007 3

Table 16 — Tin — Precision data (smoothed values)

Tin % (mass fraction)	Repeatability limit r % (mass fraction)	Reproducibility limits R_w % (mass fraction)	 R % (mass fraction)
0,003	0,000 4	0,000 7	0,000 9
0,005	0,000 6	0,001 0	0,001 2
0,01	0,000 9	0,001 3	0,001 8
0,02	0,001 4	0,001 9	0,002 8
0,05	0,002 4	0,002 9	0,004 9
0,08	0,003 1	0,003 6	0,006 6

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 document, i.e. ISO 17650:2024;

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

d) any unusual features noted during the determination;

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

Annex A
(informative)

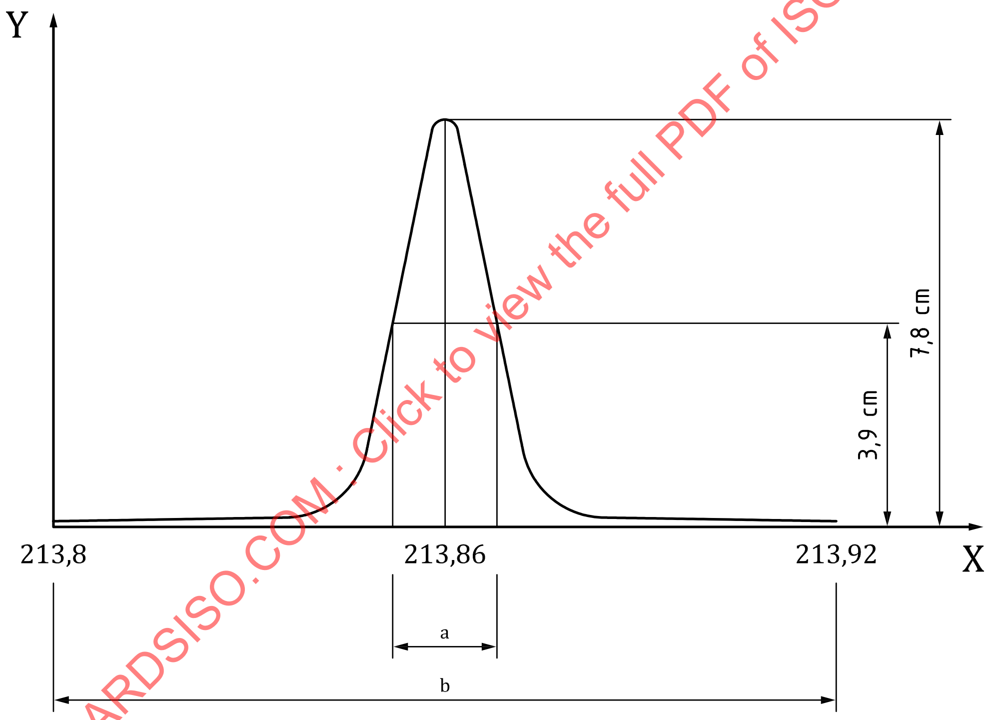
Procedure for the determination of instrumental criteria

A.1 Practical resolution of the spectrometer

Resolution is subject to theoretical definition but its practical assessment normally involves a wavelength scan across the spectral line of interest, plotting the profile, measurement of the peak width at half the peak height and calculation of the resolution in nanometres. An example is shown in Formula (A.1) and Figure A.1.

$$R_\mathrm{p} = (213{,}92 - 213{,}80) \times \frac{2}{15} = 0{,}016 \qquad \text{(A.1)}$$

where R_p is the resolution.



Key

x wavelength, nm

y intensity, au (arbitrary unit)

[a] Half peak width = 2 cm.

[b] Peak window = 15 cm.

Figure A.1 — Example of calculation of practical resolution

A.2 Minimum short-term precision

An important parameter for assessing the suitability of an instrument for a given determination is the short term stability of the emission signal, namely the closeness of agreement between the values obtained on the same test sample solution by repeating measurements in rapid succession.

It is the standard deviation of the mean results, expressed as a percentage of the concentration [relative standard deviation (RSD)].

Make ten consecutive measurements on the same solution and calculate the relative standard deviation.

A.3 Limit of detection (LOD) and limit of quantification (LOQ)

The limit of detection and limit of quantification represent two of the parameters of an analytical method. Both are derived from the standard deviation of the repeatability at a concentration level of zero.

Prepare two solutions, each containing the analyte at a concentration level of zero and ten times the estimated limit of detection respectively. These solutions should also contain concentration of acids, fusion agents and matrix elements similar to those in the samples to be analysed.

Nebulize the zero test solution for approximately 10 s and take 10 readings at the pre-set integration time. Thereafter, do the same for the solution containing a concentration of the analyte approximately 10 times the limit of detection.

From the intensity readings, calculate the mean intensities X_{10}, X_0 and the standard deviation of the zero member, s_0.

Calculate the net mean intensity ($X_{\text{n}10}$) for the solution at 10 times the limit of detection using Formula (A.2):

$$X_{\text{n}10} = X_{10} - X_0 \tag{A.2}$$

Calculate the limit of detection using Formula (A.3):

$$D_L = 4{,}65 \times s_0 \times \frac{\rho_{10}}{X_{n10}} \tag{A.3}$$

Where ρ_{10} is the concentration, expressed in mg/l, of the solution at the 10 times the limit of detection.

The limit of quantification is then given by Formula (A.4)

$$Q_L = 14{,}1 \times s_0 \times \frac{\rho_{10}}{X_{n10}} \tag{A.4}$$

Annex B
(informative)

Additional information on the precision test

The test samples used are listed in Table B.1. The detailed results obtained from the precision test are given in Tables B.2 to B.12.

Tables B.2 to B.12 were derived from the results of a precision test carried out in 2018 on steel and iron samples in 3 countries involving 11 laboratories.

The graphical representations of the precision data are given in Annex C.

Table B.1 — Test samples used

No.	ID No. and grade	C	Si	Mn	P	Cr	Ni	Cu	Mo	Co	Al	V	Ti	As	Sn
1	Cai 245 5CrMnMo	0,553	0,425	1,44	0,014	0,743	0,035	0,090	0,237	0,008 3	0,005	0,005 5	0,003 3	0,010	0,008 1
2	GBW01301 Low alloy steel	0,91	0,056	2,09	0,054	0,105	0,076	0,2	-	-	0,015	-	-	-	-
3	BH0238 Low alloy steel	1,216	0,14	0,963	0,045	0,135	2,16	0,24	0,41	-	0,438	0,061	0,327	-	-
4	GBW01305 Low alloy steel	0,035	0,59	1,79	0,089	1,03	0,02	0,46	-	-	0,59	-	-	-	-
5	GSBH40146-97 Carbon steel	0,168	0,236	0,507	0,028 6	0,018 9	0,005 1	0,009 8	-	-	-	-	-	-	-
6	GBW 01401a Pure iron	0,001 5	0,049	0,017	0,001 4	0,005 6	0,012	0,003	0,002 8	0,002 4	0,01	-	0,002 5	-	-
7	DHSE26-10 Pure iron	-	<0,000 5	0,002 2	<0,000 2	0,001 32	0,000 49	0,000 74	0,000 07	<0,000 1	0,000 23	<0,000 03	0,000 05	-	-
8	YSBC11001-99 High pure iron	0,001 6	0,001	0,006 3	0,006 4	0,003 2	0,012	0,004 4	0,002 6	0,006 3	-	-	-	-	-
9	GSBH40031-93 Trace carbon steel 10#	0,102	0,228	0,55	0,017	0,035	0,026 4	0,034	0,005 9	0,005 8	0,017	-	-	0,006 5	0,003
10	YSBC18201a-05 Low alloy steel	0,044	1,53	1,3	0,006 3	0,026	0,025	0,099	0,019	-	0,014	0,387	0,286	0,092	0,003
11	YSBC18203a-05 Low alloy steel	0,331	0,64	0,549	0,051	1,62	0,977	0,213	0,184	-	0,217	0,481	0,444	0,055	0,052
12	YSBC18207a-05 Low alloy steel	0,144	0,168	1,66	0,021	0,133	0,533	0,285	0,078	-	0,053	0,100	0,079	0,026	0,079
13	GSBH40065-93 Alloy structural steel	0,481	1,11	0,511	0,034	1,52	0,518	0,111	0,253	-	0,243	0,131	0,202	0,049	0,012
14	JSS150-18 Low alloy steel	0,495	0,201	0,101	0,039 8	0,305	4,00	0,049 1	0,196	-	0,012 4	0,019 3	-	-	-
15	JSS154-17 Low alloy steel	0,100 1	0,606	1,209	0,005 24	2,01	0,502	0,200	0,394	-	0,007 3	0,298	-	-	-
16	JSS155-16 Low alloy steel	0,039 4	0,495	0,185	0,001 8	3,00	0,153	0,398	0,705	-	0,020 0	0,403	-	-	-
17	JSS170-8 Low alloy steel	0,039 7	0,194	0,398	-	0,050 4	0,076	-	0,010 0	-	0,034	-	0,099	0,00 31	0,053 8

Table B.1 *(continued)*

No.	ID No. and grade	C	Si	Mn	P	Cr	Ni	Cu	Mo	Co	Al	V	Ti	As	Sn
18	GSB03-2456-2008 Microalloyed steel	0,001 9	1,37	0,571	0,04	0,091	0,218	0,105	0,2	0,198	-	0,009 5	0,052	0,006 9	0,000 68
19	GSB03-2455-2008 Microalloyed steel	0,256	0,077	1,10	0,025	0,322	0,086	0,201	0,094	0,092	0,045	0,023	0,111	0,015	0,008 4
20	Cai 251 Low alloy steel	0,395	0,312	0,441	0,014	1,53	0,185	0,067	0,178	0,011	-	0,002	0,004 8	0,006	0,01

Table B.2 — Data obtained from the precision test for manganese

No.	Sample	Manganese % (mass fraction)		Precision data % (mass fraction)		
		Certified	Found	Repeatability limit	Reproducibility limits	
				r	R_w	R
2	GBW01301	2,09	2,10	0,032	0,032	0,073
5	GSBH40146-97	0,507	0,503	0,007 6	0,010 5	0,017 4
6	GBW 01401a	0,017	0,017 5	0,001 5	0,001 5	0,003 0
7	DHSE26-10	0,002 2	0,002 2	0,000 5	0,001 0	0,001 6
8	YSBC11001-99	0,006 3	0,006 4	0,001 0	0,001 0	0,002 8
12	YSBC18207a-05	1,66	1,67	0,017	0,035	0,049
14	JSS150-18	0,101	0,103	0,003 6	0,003 6	0,006 5
16	JSS155-16	0,185	0,187	0,006 5	0,006 5	0,010 8
19	GSB03-2455-2008	1,10	1,10	0,018	0,043	0,058

Table B.3 — Data obtained from the precision test for phosphorus

No.	Sample	Phosphorus % (mass fraction)		Precision data % (mass fraction)		
		Certified	Found	Repeatability limit	Reproducibility limits	
				r	R_w	R
1	Cai 245	0,014	0,013 8	0,000 8	0,001 0	0,002 1
2	GBW01301	0,054	0,053 7	0,001 6	0,001 6	0,004 8
4	GBW01305	0,089	0,089 5	0,001 7	0,003 0	0,006 0
8	YSBC11001-99	0,006 4	0,006 3	0,000 5	0,000 9	0,000 9
12	YSBC18207a-05	0,021	0,020 1	0,001 4	0,001 7	0,003 1
15	JSS154-17	0,005 24	0,005 21	0,000 4	0,000 6	0,001 7

Table B.4 — Data obtained from the precision test for chromium

No.	Sample	Chromium % (mass fraction)		Precision data % (mass fraction)		
		Certified	Found	Repeatability limit	Reproducibility limits	
				r	R_w	R
1	Cai 245	0,743	0,746	0,010 3	0,013 9	0,020 8
2	GBW01301	0,105	0,107	0,003 0	0,003 9	0,008 0
4	GBW01305	1,03	1,033	0,018	0,024	0,025
5	GSBH40146-97	0,018 9	0,017 6	0,000 7	0,002	0,002
6	GBW 01401a	0,005 6	0,005 5	0,000 4	0,001 4	0,001 4
8	YSBC11001-99	0,003 2	0,003 1	0,000 6	0,000 8	0,001 5
14	JSS150-18	0,305	0,309	0,005 9	0,013 2	0,016 0
15	JSS154-17	2,01	2,006	0,024	0,035	0,065
16	JSS155-16	3,00	2,998	0,064	0,077	0,117
17	JSS170-8	0,050 4	0,050 3	0,001 2	0,002 0	0,003 0

Table B.5 — Data obtained from the precision test for nickel

No.	Sample	Nickel % (mass fraction)		Precision data % (mass fraction)		
		Certified	Found	Repeatability limit *r*	Reproducibility limits R_w	 *R*
3	BH0238	2,16	2,162	0,015	0,100	0,103
5	GSBH40146-97	0,005 1	0,004 9	0,000 5	0,000 8	0,002 0
8	YSBC11001-99	0,012	0,011 7	0,001 7	0,001 7	0,003 2
10	YSBC18201a-05	0,025	0,023 9	0,001 5	0,001 5	0,004 1
11	YSBC18203a-05	0,977	0,980	0,022	0,022	0,033
14	JSS150-18	4,00	4,015	0,065	0,127	0,145
15	JSS154-17	0,502	0,498	0,010 0	0,012 8	0,024 5
16	JSS155-16	0,153	0,151	0,004 3	0,005 2	0,010 9
17	JSS170-8	0,076	0,074 4	0,002 7	0,002 9	0,007 0

Table B.6 — Data obtained from the precision test for molybdenum

No.	Sample	Molybdenum % (mass fraction)		Precision data % (mass fraction)		
		Certified	Found	Repeatability limit *r*	Reproducibility limits R_w	 *R*
3	BH0238	0,41	0,407	0,010	0,010	0,017
6	GBW 01401a	0,002 8	0,002 7	0,000 5	0,000 5	0,001 2
9	GSBH40031-93	0,005 9	0,005 6	0,000 6	0,000 7	0,001 2
10	YSBC18201a-05	0,019	0,017 5	0,001 1	0,001 2	0,002 7
12	YSBC18207a-05	0,078	0,075 0	0,001 4	0,003 2	0,007 1
14	JSS150-18	0,196	0,200	0,007	0,007	0,012
16	JSS155-16	0,705	0,701	0,013	0,018	0,022
17	JSS170-8	0,010 0	0,010 2	0,000 8	0,001 3	0,002 4
19	GSB03-2455-2008	0,094	0,093 5	0,002 1	0,003 6	0,005 8

Table B.7 — Data obtained from the precision test for arsenic

No.	Sample	Arsenic % (mass fraction)		Precision data % (mass fraction)		
		Certified	Found	Repeatability limit *r*	Reproducibility limits R_w	 *R*
1	Cai 245	0,010	0,009 6	0,000 8	0,001 5	0,002 6
9	GSBH40031-93	0,006 5	0,006 3	0,000 6	0,001 0	0,001 7
10	YSBC18201a-05	0,092	0,090 9	0,001 3	0,002 9	0,005 4
12	YSBC18207a-05	0,026	0,025 7	0,001 2	0,002 1	0,003 2
13	GSBH40065-93	0,049	0,049 9	0,001 7	0,001 7	0,007 6
17	JSS170-8	0,003 1	0,003 0	0,000 4	0,000 8	0,001 2

Table B.8 — Data obtained from the precision test for cobalt

No.	Sample	Cobalt % (mass fraction)		Precision data % (mass fraction)		
		Certified	Found	Repeatability limit	Reproducibility limits	
				r	R_w	R
1	Cai 245	0,008 3	0,008 2	0,000 3	0,000 8	0,001 3
6	GBW 01401a	0,002 4	0,002 2	0,000 5	0,000 5	0,001 2
9	GSBH40031-93	0,005 8	0,005 8	0,000 2	0,000 3	0,001 0
18	GSB03-2456-2008	0,198	0,199	0,004 4	0,005 5	0,013 4
19	GSB03-2455-2008	0,092	0,095 6	0,001 8	0,004 0	0,007 2
20	Cai 251	0,011	0,010 9	0,000 4	0,000 9	0,001 6

Table B.9 — Data obtained from the precision test for copper

No.	Sample	Copper % (mass fraction)		Precision data % (mass fraction)		
		Certified	Found	Repeatability limit	Reproducibility limits	
				r	R_w	R
4	GBW01305	0,46	0,462	0,013 2	0,015 8	0,030 1
5	GSBH40146-97	0,009 8	0,009 2	0,000 5	0,000 6	0,001 8
6	GBW 01401a	0,003	0,002 8	0,000 5	0,000 6	0,001 3
8	YSBC11001-99	0,004 4	0,004 3	0,000 7	0,000 7	0,001 8
9	GSBH40031-93	0,034	0,033 6	0,000 5	0,002 0	0,003 1
14	JSS150-18	0,049 1	0,049 6	0,001 3	0,002 0	0,003 0
15	JSS154-17	0,200	0,200	0,009 0	0,009 0	0,014 3
18	GSB03-2456-2008	0,105	0,104	0,001 7	0,005 7	0,006 9

Table B.10 — Data obtained from the precision test for tin

No.	Sample	Tin % (mass fraction)		Precision data % (mass fraction)		
		Certified	Found	Repeatability limit	Reproducibility limits	
				r	R_w	R
1	Cai 245	0,008 1	0,008 3	0,000 8	0,000 8	0,001 0
9	GSBH40031-93	0,003 0	0,003 1	0,000 4	0,001 0	0,001 0
12	YSBC18207a-05	0,079	0,079 6	0,003 7	0,004 2	0,006 9
13	GSBH40065-93	0,012	0,011 6	0,001 1	0,001 4	0,002 8
17	JSS170-8	0,053 8	0,053 1	0,002 0	0,002 8	0,004 9

Table B.11 — Data obtained from the precision test for titanium

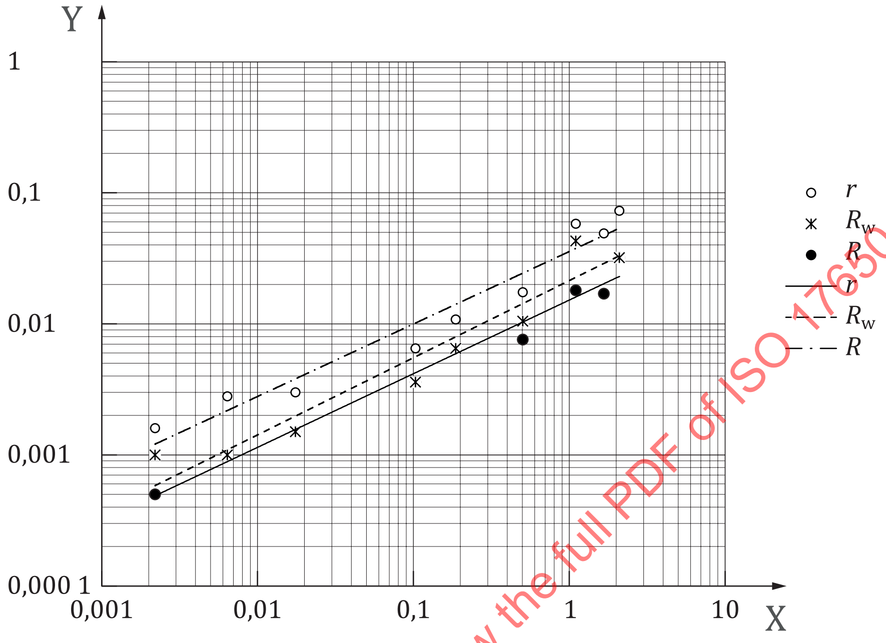
No.	Sample	Titanium % (mass fraction)		Precision data % (mass fraction)		
		Certified	Found	Repeatability limit	Reproducibility limits	
				r	R_w	R
1	Cai 245	0,003 3	0,003 35	0,000 2	0,000 4	0,000 4
6	GBW 01401a	0,002 5	0,002 48	0,000 2	0,000 3	0,000 8
11	YSBC18203a-05	0,444	0,433	0,006 4	0,013 3	0,033 4
13	GSBH40065-93	0,202	0,202	0,004 7	0,004 7	0,010 4
17	JSS170-8	0,099	0,099 1	0,001 2	0,005 6	0,005 8
18	GSB03-2456-2008	0,052	0,051 7	0,000 9	0,004 8	0,004 8
19	GSB03-2455-2008	0,111	0,109	0,002 6	0,007 9	0,010 6
20	Cai 251	0,004 8	0,004 9	0,000 3	0,000 5	0,000 6

Table B.12 — Data obtained from the precision test for vanadium

No.	Sample	Vanadium % (mass fraction)		Precision data % (mass fraction)		
		Certified	Found	Repeatability limit	Reproducibility limits	
				r	R_w	R
1	Cai 245	0,005 5	0,006 0	0,000 2	0,000 6	0,001 8
3	BH0238	0,061	0,061 5	0,001 2	0,002 7	0,011 0
11	YSBC18203a-05	0,481	0,482	0,014 1	0,014 1	0,027 5
12	YSBC18207a-05	0,100	0,101	0,003 0	0,005 7	0,008 6
14	JSS150-18	0,019 3	0,019 4	0,000 4	0,001 1	0,001 6
15	JSS154-17	0,298	0,299	0,004 3	0,005 9	0,018 5
18	GSB03-2456-2008	0,009 5	0,008 9	0,000 4	0,000 7	0,002 0
20	Cai 251	0,002	0,002 4	0,000 3	0,000 5	0,001 3

Annex C
(informative)

Graphical representation of precision data



Key

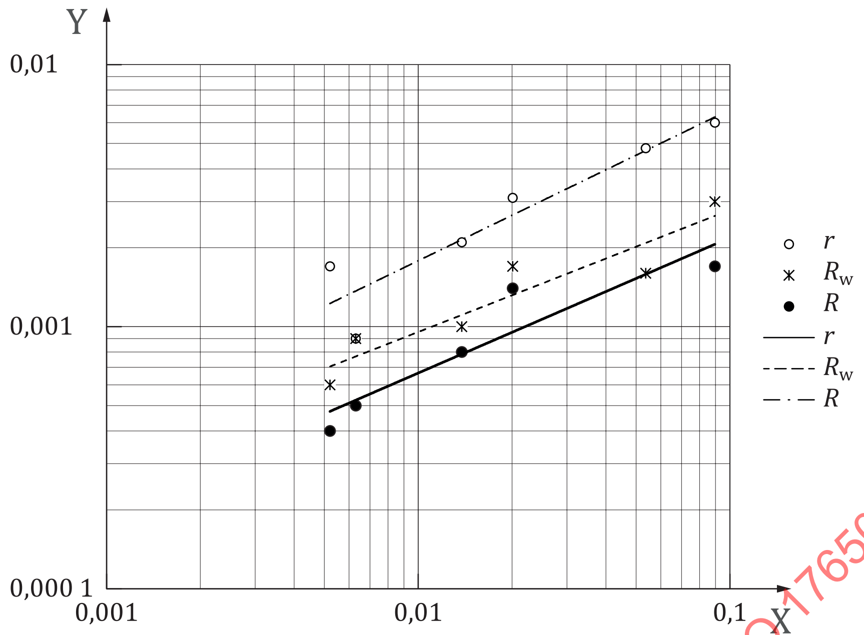
X	manganese contents, % (mass fraction)
Y	precision, % (mass fraction)
r	repeatability
R_w	within-laboratory reproducibility
R	reproducibility

$\lg r = 0{,}570\,4 \lg m -1{,}815\,1$ $R^2=0{,}982\,3$

$\lg R_w = 0{,}595\,9 \lg m -1{,}667\,6$ $R^2=0{,}940\,2$

$\lg R = 0{,}552\,4 \lg m -1{,}447\,4$ $R^2=0{,}947\,5$

Figure C.1 — Logarithmic relationship between manganese content (*m*) and repeatability limit (*r*) and reproducibility limits (R_w and *R*)



Key

X phosphorus contents, % (mass fraction)

Y precision, % (mass fraction)

r repeatability

R_w within-laboratory reproducibility

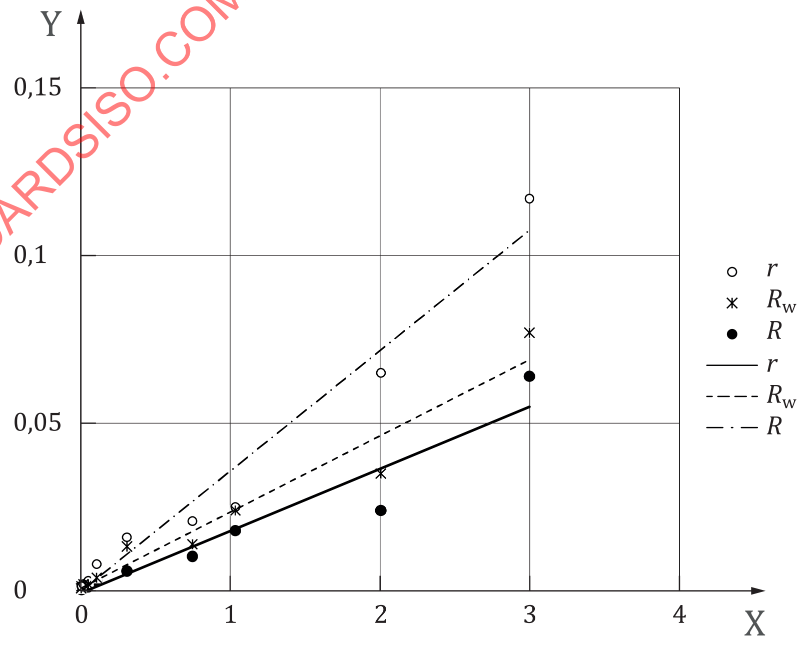
R reproducibility

$\lg r = 0{,}484\ 6 \lg m - 2{,}185\ 2$ $R^2 = 0{,}882\ 5$

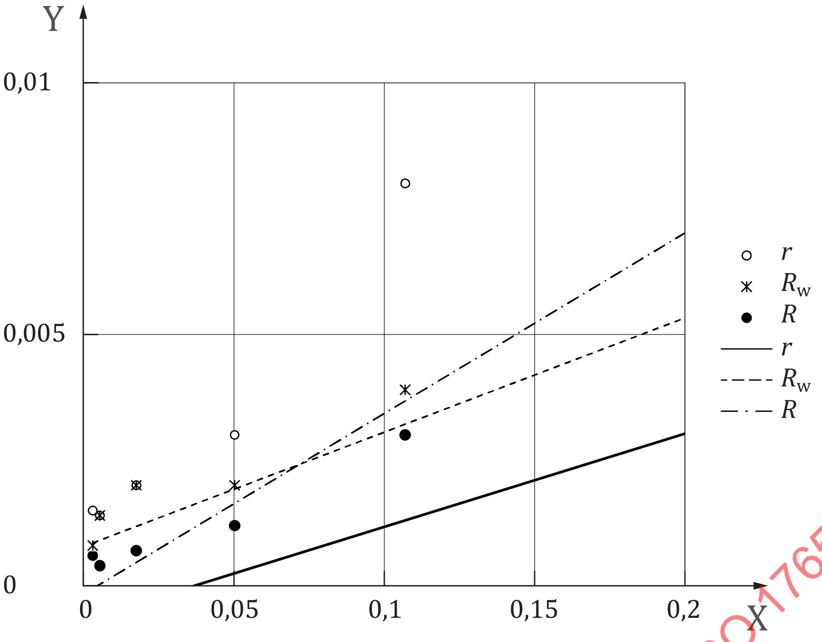
$\lg R_w = 0{,}459\ 6 \lg m - 2{,}098\ 0$ $R^2 = 0{,}849\ 7$

$\lg R = 0{,}571\ 8 \lg m - 1{,}601\ 9$ $R^2 = 0{,}892\ 1$

Figure C.2 — Logarithmic relationship between phosphorus content (*m*) and repeatability limit (*r*) and reproducibility limits (R_w and *R*)



a) Figure of the entire application range



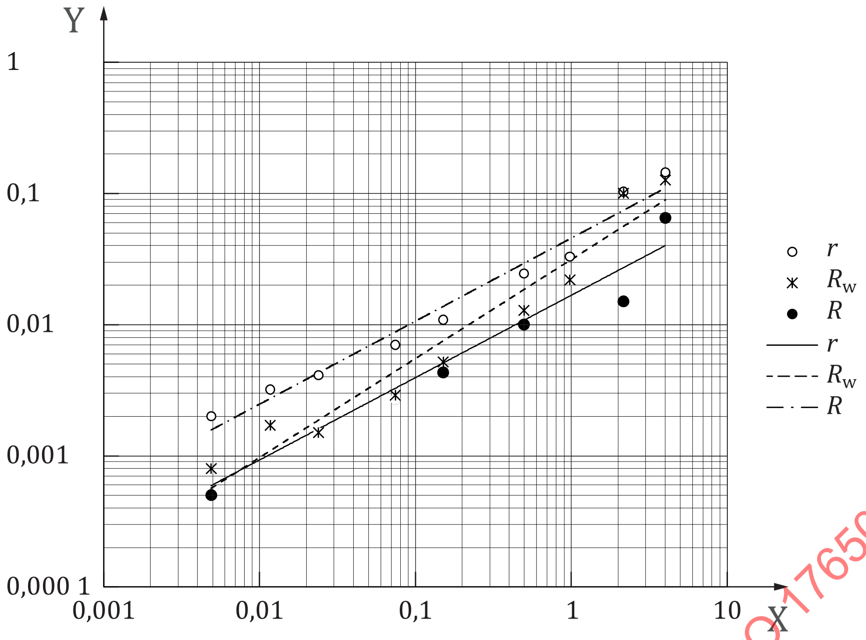
b) Enlarged figure for the range of <0,2 % (mass fraction)

Key

X chromium contents, % (mass fraction)
Y precision, % (mass fraction)
r repeatability
R_w within-laboratory reproducibility
R reproducibility

$r = 0{,}016\,58\,m + 0{,}000\,44$	$R^2=0{,}929\,8$
$R_w = 0{,}023\,93\,m + 0{,}001\,0$	$R^2=0{,}954\,3$
$R = 0{,}035\,31\,m + 0{,}001\,4$	$R^2=0{,}969\,5$

Figure C.3 — Linear relationship between chromium content (m) and repeatability limit (r) and reproducibility limits (R_w and R)



Key

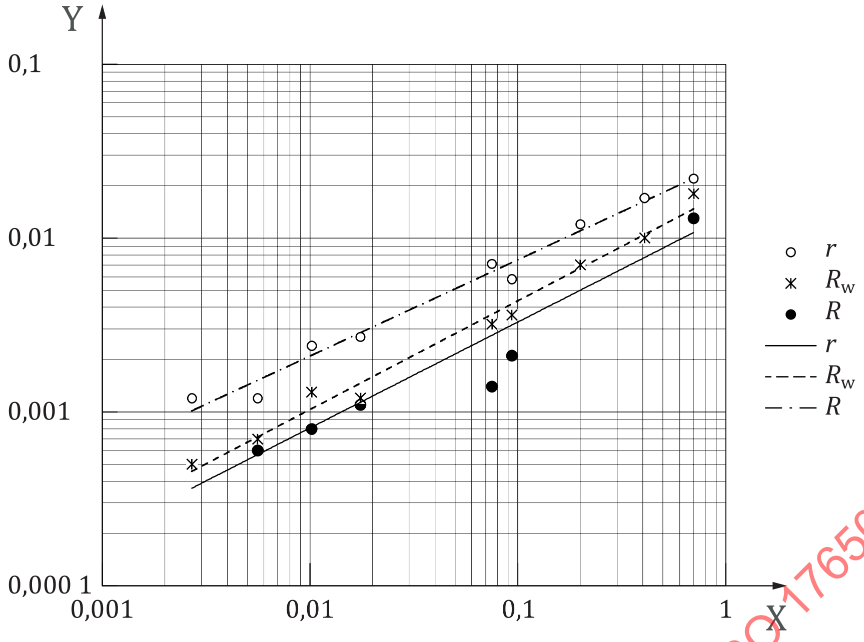
X	nickel contents, % (mass fraction)
Y	precision, % (mass fraction)
r	repeatability
R_w	within-laboratory reproducibility
R	reproducibility

$\lg r = 0,626\,6 \lg m -1,773\,1$ $R^2=0,946\,8$

$\lg R_w = 0,750\,8 \lg m -1,502\,6$ $R^2=0,948\,6$

$\lg R = 0,634\,4 \lg m -1,340\,4$ $R^2=0,973\,3$

Figure C.4 — Logarithmic relationship between nickel content (m) and repeatability limit (r) and reproducibility limits (R_w and R)



Key

X molybdenum contents, % (mass fraction)

Y precision, % (mass fraction)

r repeatability

R_w within-laboratory reproducibility

R reproducibility

$\lg r = 0{,}616\,1 \lg m -1{,}872\,9$	$R^2=0{,}932\,0$
$\lg R_w = 0{,}639\,2 \lg m -1{,}726\,2$	$R^2=0{,}985\,4$
$\lg R = 0{,}559\,8 \lg m -1{,}559\,5$	$R^2=0{,}983\,2$

Figure C.5 — Logarithmic relationship between molybdenum content (*m*) and repeatability limit (*r*) and reproducibility limits (R_w and *R*)