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Chemical analysis of ferrous materials — Inductively coupled plasma optical emission spectrometric analysis of unalloyed and low alloyed steels — Determination of Si, Mn, P, Cu, Ni, Cr, Mo and Sn, following dissolution with nitric and sulphuric acids [Routine method]

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National foreword

This British Standard is the UK implementation of EN 10355:2013.

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A list of organizations represented on this committee can be obtained on request to its secretary.

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Chemical analysis of ferrous materials - Inductively coupled plasma optical emission spectrometric analysis of unalloyed and low alloyed steels - Determination of Si, Mn, P, Cu, Ni, Cr, Mo and Sn, following dissolution with nitric and sulphuric acids [Routine method]

Analyse chimique des matériaux ferreux - Analyse des aciers non alliés et faiblement alliés par spectrométrie d'émission optique avec source à plasma induit - Détermination de Si, Mn, P, Cu, Ni, Cr, Mo et Sn, après mise en solution par les acides nitrique et sulfurique [Méthode de routine]

Chemische Analyse von Eisenwerkstoffen - Analyse von unlegierten und niedrig legierten Stählen mittels optischer Emissionsspektrometrie mit induktiv gekoppeltem Plasma - Bestimmung von Si, Mn, P, Cu, Ni, Cr, Mo und Sn nach Lösen in Salpeter- und Schwefelsäure [Routineverfahren]

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Foreword

This document (EN 10355:2013) has been prepared by Technical Committee ECISS/TC 102 “Methods of chemical analysis for iron and steel”, the secretariat of which is held by SIS.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2014, and conflicting national standards shall be withdrawn at the latest by February 2014.

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1 Scope

This European Standard specifies an inductively coupled plasma optical emission spectrometry routine method for the analysis of unalloyed and low alloyed steels, whose iron content shall be at least 95 %. This standard differs from the similar standard EN 10351:2011 in that it is optimised for the determination of silicon.

This method is applicable to the elements listed in Table 1 within the ranges shown.

The sample preparation described may not completely dissolve samples having a combination of high chromium and substantial carbon. Incomplete dissolution may also affect the determination of manganese and molybdenum in these samples. For this reason, the scope of the method is limited to chromium contents ≤ 0,9 %, whereas the scope of EN 10351 covers a range of up to 1,6 % chromium.

Table 1 — Application ranges

Element	Mass fraction %	
	min.	max.
Si	0,020	0,45
Mn	0,005	1,40
P	0,005	0,10
Cu	0,005	0,60
Ni	0,010	2,00
Cr	0,010	0,90
Mo	0,005	0,60
Sn	0,010	0,10

NOTE For tin, see NOTE 2 under Clause 11.

In all cases, the ranges specified can be extended or adapted (after validation) for the determination of other mass fractions, provided that the iron content in the samples under concern is above 95 %.

Other elements may be included. However such elements and their mass fractions should be carefully checked, taking into account the possible interferences, the sensitivity, the resolution and the linearity criteria of each instrument and each wavelength.

Depending also on the sensitivity of each instrument, suitable dilutions of the calibration and the test sample solutions may be necessary.

Moreover, even if the method described is "multi elemental", it is not absolutely necessary to carry out the determination of all the elements of its scope simultaneously. The measurement conditions have to be optimised by each laboratory, depending on the performances of each apparatus available.

2 Normative references

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

EN ISO 648, *Laboratory glassware — Single-volume pipettes (ISO 648)*

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

3 Principle

Dissolution of a test portion with a nitric-sulphuric acids mixture. Addition of an ammonium peroxodisulphate solution and boiling. After cooling, addition of a hydrogen peroxide solution.

After suitable dilution and, if necessary, addition of an internal reference element, nebulisation of the solution into an inductively coupled plasma optical emission spectrometer and measurement of the intensity of the emitted light from each element (including, where relevant, the intensity of the internal reference element).

4 Reagents

During the analysis, use only reagents of recognised analytical grade and only distilled water or water of equivalent purity.

The same reagents should be used for the preparation of calibration solutions and of sample solutions.

4.1 Hydrochloric acid, HCl (ρ_{20} = 1,19 g/ml).

4.2 Hydrochloric acid, solution 1 + 1.

Add 500 ml of hydrochloric acid (4.1) to 500 ml of water.

4.3 Nitric acid, HNO_3 (ρ_{20} = 1,33 g/ml).

4.4 Nitric acid, solution 1 + 1.

Add 500 ml of nitric acid (4.3) to 500 ml of water.

4.5 Sulphuric acid, H_2SO_4 (ρ_{20} = 1,84 g/ml).

4.6 Hydrogen peroxide, H_2O_2 30 % (mass fraction) solution.

4.7 Hydrogen peroxide, H_2O_2 3 % (mass fraction) solution.

Dilute 50 ml of hydrogen peroxide (4.6) with water to 500 ml.

4.8 Nitric-sulphuric acids mixture.

Add to approximately 500 ml of water 50 ml of nitric acid (4.3) and 50 ml of sulphuric acid (4.5) and mix. After cooling, dilute to 1 l with water and mix.

4.9 Ammonium peroxodisulphate solution, 20 g/l.

Dissolve 10 g of ammonium peroxodisulphate in 500 ml water.

4.10 Chromium 1 g/l standard solution.

Weigh (0,5 ± 0,001) g of chromium (99,99 % purity) and transfer into a 250 ml beaker. Add 40 ml of hydrochloric acid (4.1) and heat gently until chromium is completely dissolved. After cooling, transfer the solution quantitatively into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this solution contains 1 mg of Cr.

4.11 Copper 1 g/l standard solution.

Weigh (0,5 ± 0,001) g of copper (99,99 % purity) and transfer into a 250 ml beaker. Dissolve it in 10 ml of nitric acid solution (4.4). Heat gently until the metal is dissolved and then boil until nitrous fumes have been expelled. After cooling, transfer the solution quantitatively into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this solution contains 1 mg of Cu.

4.12 Manganese 1 g/l standard solution.

The manganese used to prepare the solution is released from superficial oxide possibly present by introducing a few grams of metal in a 250 ml beaker containing (150 to 160) ml of water and (15 to 20) ml of sulphuric acid (4.5). Shake and after a few seconds, allow the solution to settle and add water. Repeat the water cleaning several times. Remove the metallic manganese and rinse with acetone. Dry the metal in an oven at 100 °C for 2 min or with a hair dryer. Cool in a desiccator.

Weigh (0,5 ± 0,001) g of this purified manganese and transfer into a 250 ml beaker. Dissolve it in 5 ml of hydrochloric acid (4.1) and 10 ml of nitric acid solution (4.4). Heat gently until the metal is dissolved. After cooling, transfer the solution quantitatively into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this solution contains 1 mg of Mn.

4.13 Molybdenum 1 g/l standard solution.

Weigh (0,5 ± 0,001) g of molybdenum (99,99 % purity) and transfer into a 250 ml beaker. Dissolve it in 10 ml of hydrochloric acid (4.1) and 10 ml of nitric acid (4.3). Heat gently until the metal is dissolved. After cooling, transfer the solution quantitatively into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this solution contains 1 mg of Mo.

4.14 Nickel 1 g/l standard solution.

Weigh (0,5 ± 0,001) g of nickel (99,99 % purity) and transfer into a 250 ml beaker. Dissolve it in 10 ml of nitric acid solution (4.4). Heat gently until the metal is dissolved, and then boil until nitrous fumes have been expelled. After cooling, transfer the solution quantitatively into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this solution contains 1 mg of Ni.

4.15 Phosphorus 1 g/l standard solution.

Weigh (2,197 ± 0,001) g of dried potassium dihydrogen phosphate, transfer into a 250 ml beaker and dissolve it with water. Transfer the solution quantitatively into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this solution contains 1 mg of P.

4.16 Silicon 1 g/l standard solution.

Using a suitable plastic beaker, dissolve (3,171 ± 0,001) g of dried ammonium hexafluorosilicate $[(NH_4)_2SiF_6]$ in hot water (~ 80 °C).

Allow to cool and transfer the solution quantitatively into a polyethylene 500 ml one-mark volumetric flask, dilute to the mark with water and mix well.

1 ml of this solution contains 1 mg of Si.

4.17 Tin 1 g/l standard solution [freshly prepared].

Weigh (0,5 ± 0,001) g of tin (99,99 % purity) and transfer into a 250 ml beaker. Dissolve it in 50 ml of hydrochloric acid (4.1). Heat gently until the metal is dissolved. After cooling, transfer the solution quantitatively into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this solution contains 1 mg of Sn.

NOTE Standard solutions whose preparations are described in 4.10 to 4.17 can be replaced by commercially available standard solutions, provided that they are supplied by a recognised producer and their traceability fully documented.

4.18 Internal reference element solution, 1 g/l.

Choose a suitable element to be added as internal reference and prepare a 1 g/l solution.

NOTE Elements such as Sc and Y are often used for this purpose.

4.19 Pure iron.

The iron selected shall have a content of less than one tenth of the lower limit of each element as given in the scope.

5 Apparatus

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

5.1 Microwave system.

5.2 Gravimetric or volumetric dispensers.

5.3 Optical emission spectrometer, equipped with inductively coupled plasma.

This shall be equipped with a nebulisation system. The instrument used will be satisfactory if, after optimising in accordance with the manufacturer’s instructions, it meets the performance criteria given in Annex A.

6 Sampling

Sampling shall be carried out in accordance with EN ISO 14284 or with an appropriate national standard for steel.

7 Sample solution preparation

7.1 General

The method is optimised for use with automated systems, **open** microwave digestion units (5.1) and gravimetric dispensers (5.2).

NOTE This method was also tested with closed microwave units, after a suitable optimisation of the relevant operating conditions: temperatures and times.

The method can also be used in a classical way with hot plates and manual additions.

7.2 Test portion

Weigh, to the nearest 1 mg, 250 mg of the test sample.

7.3 Preparation of the test solution

7.3.1 Automated system, OPEN units

Transfer the test portion (7.2) into a PTFE tube.

Add 10 g of the nitric-sulphuric acid mixture (4.8) and cover with a suitable cover (PTFE or some other microwave transparent material, perfectly clean and free from contamination. Screw caps shall be avoided with open microwave units). Use the microwave to heat the sample at about 120 °C for 7 min and then allow to cool for about 10 min.

Add 5 g of the ammonium peroxodisulphate solution (4.9), and cover. Heat at about 120 °C for 3 min by means of the microwave system, and then allow to cool for about 10 min.

Add 5 g of the hydrogen peroxide solution (4.7) and mix well. Cool for about 10 min.

The cooling time may be increased to ensure that gas evolution has ceased before analysing the sample.

The addition of 2 g HCl (4.1) may help to prevent the hydrolysis of silicon and tin.

If an internal reference element is used, add a suitable quantity of the internal reference solution (4.18), dilute the sample solution to 50 g, weighted to the nearest mg and mix well.

If necessary, filter the solution through a dry close-texture filter paper. Reject the first portions of the filtrate.

It is recommended to carry out the measurements on freshly prepared solutions, in order to avoid silicon hydrolysis.

7.3.2 Manual procedure

Transfer the test portion (7.2) into a 100 ml quartz or glassware conical flask (or in a 100 ml PTFE beaker).

NOTE It has been shown that perfectly clean quartz or ordinary glass conical flasks are suitable even for the determination of silicon.

Other plastic materials may be used, provided that they are heat resistant and free from contamination.

Add 10 ml of the nitric-sulphuric acid mixture (4.8). If beakers are used, cover with a PTFE[1] watch glass and heat until gently boiling (the hotplate temperature shall be adjusted in order to allow a gentle boiling of the sample solution). Maintain the boiling for about 7 min to 10 min and then allow to cool for about 10 min.

Add 5 ml of the ammonium peroxodisulphate solution (4.9), cover and heat until gently boiling. Maintain the boiling for about 3 min to 5 min and then allow to cool for about 10 min.

Add 5 ml of the hydrogen peroxide solution (4.7) and mix well. Cool for about 10 min.

The cooling time may be increased to ensure that gas evolution has ceased before analysing the sample.

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[1] Covers made from other materials can be suitable, provided that these materials are free from contamination.

Transfer the sample solution into a 50 ml one-mark volumetric flask and then, if an internal reference element is used, add, with a calibrated pipette, a suitable volume of the internal reference element solution (4.18).

The addition of 2 ml HCl (4.1) may help to prevent the hydrolysis of silicon and tin.

Dilute to the mark with water and mix well.

If necessary, filter the solution through a dry close-texture filter paper. Reject the first portions of the filtrate.

It is recommended to carry out the measurements on freshly prepared solutions, in order to avoid silicon hydrolysis.

8 Calibration process

8.1 Steps

The calibration process is subdivided into calibration and drift compensation by re-calibration.

8.2 Preparation of the multi-elemental calibration solutions

Weight 2,500 g of pure iron (4.19) into a 500 ml beaker and add 100 ml of the nitric-sulphuric acids mixture (4.8). Heat at about 120 °C, for 7 min.

Add 50 ml of the ammonium peroxodisulphate solution (4.9), cover and heat at about 120 °C for 3 min. Boil gently and allow to cool.

Add 50 ml of the hydrogen peroxide solution (4.7) and mix well. Transfer into a 250 ml one-mark volumetric flask, dilute to the mark with water and mix well.

Into each of a series of four 100 ml one-mark volumetric flasks transfer 50,0 ml of this iron solution and, with calibrated pipettes, add the volumes of the mono-elemental standard solutions (4.10 to 4.17) or of commercial available mono-elemental standard solutions shown in Table 2.

If an internal reference element is used add, with a calibrated pipette a suitable volume of the internal reference element solution (4.18); this volume shall be double of that added to the sample solution (7.3).

The addition of 4 ml HCl (4.1) may help to prevent the hydrolysis of silicon and tin.

Dilute to the mark and mix well.

It is recommended to carry out the inductively coupled plasma optical emission spectrometric measurements on freshly prepared solutions, in order to avoid silicon hydrolysis.

In a fifth 100 ml one-mark volumetric flasks transfer 50,0 ml of the above 10 g/l iron solution. Dilute to the mark and mix well.

Use this solution to test whether or not the lowest concentration of each element is high enough to be considered as "different from the zero point".

Strong care should be taken in order to ensure that the quantity of acids in the calibration solutions (**particularly when commercially available standard solutions are used**), in the sample solutions and in the Certified Reference Materials solutions prepared to check the trueness of the calibration remain the same.

The calibration curves obtained may be stored within a computer, connected to the inductively coupled plasma optical emission spectrometer.

The trueness of these calibration functions should be verified by measuring at least two suitable Certified Reference Materials or Internal Reference Materials sample solutions (just above the low point and just below the high point of each calibration range).

Table 2 — Composition of the multi-elemental calibration solutions

Element	Label			
	F1	F2	F3	F4
Si (4.16)	0,1 mg [0,02 %] [a]	0,25 mg [0,05 %] [b]	2,25 mg [0,45 %] [c]	0,5 mg [0,1 %] [d]
Mn (4.12)	7 mg [1,4 %] 7 ml	1 mg [0,2 %] 1 ml	0,025 mg [0,005 %] [e]	0,1 mg [0,02 %] [f]
P (4.15)	0,025 mg [0,005 %] [g]	0,05 mg [0,01 %] [h]	0,25 mg [0,05 %] [i]	0,5 mg [0,1 %] [j]
Cu (4.11)	0,25 mg [0,05 %] [k]	3,0 mg [0,6 %] 3 ml	0,025 mg [0,005 %] [l]	0,5 mg [0,1 %] [m]
Ni (4.14)	10 mg [2,0 %] 10 ml	2,5 mg [0,5 %] 2,5 ml	0,05 mg [0,01 %] [n]	0,25 mg [0,05 %] [o]
Cr (4.10)	0,05 mg [0,01 %] [p]	0,25 mg [0,05 %] [q]	4,5 mg [0,9 %] 4,5 ml	2,5 mg [0,5 %] 2,5 ml
Mo (4.13)	0,05 mg [0,01 %] [r]	0,25 mg [0,05 %] [s]	3 mg [0,6 %] 3 ml	0,5 mg [0,1 %] [t]
Sn (4.17)	0,5 mg [0,1 %] [u]	0,05 mg [0,01 %] [v]	0,25 mg [0,05 %] [w]	0,1 mg [0,02 %] [x]

[a] 1 ml of a 0,1 g/l silicon standard solution

[b] 2,5 ml of a 0,1 g/l silicon standard solution

[c] 22,5 ml of a 0,1 g/l silicon standard solution

[d] 5,0 ml of a 0,1 g/l silicon standard solution

[e] 2,5 ml of a 0,01 g/l manganese standard solution

[f] 10 ml of a 0,01 g/l manganese standard solution

[g] 2,5 ml of a 0,01 g/l phosphorus standard solution

[h] 5,0 ml of a 0,01 g/l phosphorus standard solution

[i] 2,5 ml of a 0,1 g/l phosphorus standard solution

[j] 5,0 ml of a 0,1 g/l phosphorus standard solution

[k] 2,5 ml of a 0,1 g/l copper standard solution

[l] 2,5 ml of a 0,01 g/l copper standard solution

[m] 5,0 ml of a 0,1 g/l copper standard solution

[n] 5,0 ml of a 0,01 g/l nickel standard solution

[o] 2,5 ml of a 0,1 g/l nickel standard solution

[p] 2,5 ml of a 0,01 g/l chromium standard solution

[q] 2,5 ml of a 0,1 g/l chromium standard solution

[r] 5,0 ml of a 0,01 g/l molybdenum standard solution

[s] 2,5 ml of a 0,1 g/l molybdenum standard solution

[t] 5,0 ml of a 0,1 g/l molybdenum standard solution

[u] 5,0 ml of a 0,1 g/l tin standard solution

[v] 5,0 ml of a 0,01 g/l tin standard solution

[w] 2,5 ml of a 0,1 g/l tin standard solution

[x] 10,0 ml of a 0,01 g/l tin standard solution

8.3 Re-calibration

Drifts in the spectrometer readings shall be corrected by using the re-calibration procedure as described in the manufacturer's instruction manual.

For that purpose the synthetic multi-elemental solutions (8.2), used for the calibration or suitable Certified Reference Materials or Internal Reference Materials solutions may be used.

It is strongly recommended to carry out a re-calibration of the instrument before the analysis of each set of unknown samples.

9 Determination

9.1 Synoptic

The synoptic of the operations described in this paragraph is given in Annex B.

9.2 Adjustment of the spectrometer

Start the inductively coupled plasma optical emission spectrometer and let it stabilise in accordance with the manufacturer's instructions before taking any measurements.

At the wavelengths of the analytical lines specified in Table 3, adjust all relevant instrumental parameters, as well as the pre-spraying and the integrating times, according to the instrument manufacturer's instructions while aspirating (for each element) the highest concentration calibration solution.

Table 3 — Wavelengths for determinations related with unalloyed and low alloyed steels

Element	Wavelength (nm)
Si	185,0 or 251,6 or 288,2
Mn	257,6 or 293,1 or 403,08
P	178,2 or 178,3
Cu	217,9 or 324,7 or 327,4
Ni	222,5 or 230,3 or 231,6
Cr	205,6 or 206,6 or 267,7 or 285,0
Mo	202,0 or 204,05 or 281,6
Sn	189,9 or 190,0
Sc	*361,4*
Y	*371,0*

Depending on the instrument configuration these parameters may include the outer, intermediate or central gas flow-rates, the torch position, the entrance slits, the exit slits and the photomultiplier tubes voltage.

Other wavelengths may be used, provided that interferences, sensitivity, resolution and linearity criteria have been carefully investigated.

Prepare the software for measurements of the intensity, and for the calculation of the mean value and relative standard deviation corresponding to each analytical line.

Each time the internal reference element is used, prepare the software to calculate the ratio between the intensity of each analyte and the intensity of the internal reference element.

9.3 Spectrometric measurements of the calibration solutions

Carry out the spectrometric measurements of the calibration solutions (8.2). A simultaneous spectrometer shall be available for measurements using the internal reference element (ratio mode).

For each calibration solution, three to five integrations are necessary in order to calculate the mean intensities or the mean ratioed intensities.

Establish the calibration curves using the measured mean intensities or ratioed mean intensities and the corresponding analyte amounts, expressed in percentage (mass fraction).

Use software suitable for regression calculations and calculate the corresponding correlation coefficients: these coefficients shall be, at least, 0,999.

If this criterion is not conforming, check discrepancies within the multi-elemental standard solutions preparation, or adapt the analytical range(s) either by performing suitable dilutions of the calibration standard solutions or by adapting the analytical range itself.

If some calibration curves are second degree mathematical functions within the range of content, the number of multi-elemental calibration solution should be increased.

The trueness of these calibration functions shall be verified by measuring at least two suitable Certified Reference Materials (or Internal Reference Materials) sample solutions (just above the low point and just below the high point of each calibration range).

The differences between the measured values and the reference values shall not exceed either the interval "Certified value ± 2 times the corresponding standard deviation" or the limits given in Table 4, or when appropriate, the limits fixed by suitable control charts (SPC).

If these criteria are not met, repeat the test with a re-prepared set of mono-elemental calibration solutions or adapt the analytical range(s).

Table 4 — Trueness control limits

Content range %	Maximum difference (±) %
0,001 to 0,002	0,000 5
0,002 to 0,005	0,000 9
0,005 to 0,01	0,001 4
0,01 to 0,02	0,002 2
0,02 to 0,05	0,004 0
0,05 to 0,1	0,006 0
0,1 to 0,2	0,009 0
0,2 to 0,5	0,016
0,5 to 1,0	0,025
1,0 to 2,0	0,040

9.4 Analysis

9.4.1 Main steps

Carry out the analysis by following the steps described here below.

9.4.2 Re-calibration

Start each analytical series by a re-calibration of the instrument. Check the performance of this operation for each element to be determined by measuring at least one Certified Reference Material (CRM 1) or one Internal Reference Material (IRM 1) sample solution, prepared as described in Clause 7.

Check the results: the re-calibration will be acceptable if all the results for the Certified Reference Material (or Internal Reference Material) concerned are situated in the interval "Certified Value ± 2σ", where σ is the standard deviation of the certified value.

If abnormal deviations appear, restart the re-calibration procedure.

This sample solution (CRM 1 or IRM 1) can also be used for all the drift controls to be carried out during the analytical series measurements.

9.4.3 Assessment of trueness

Analyse two other Certified Reference Materials (CRM 2 and CRM 3), whose compositions should be as near as possible to that of the unknown samples.

NOTE In cases where suitable Certified Reference Materials are not available, Internal Reference Materials can be used, provided their homogeneity has been carefully checked and that they have been analysed under "referee basis".

Check the results: the measurement of the unknown samples may commence if the results for at least one of the Certified Reference Materials concerned are situated in the interval "Certified Value ± 2σ".

If unacceptable results are obtained for the same element in both CRM solutions then reject all of the sample solutions and re-commence the sample preparation.

9.4.4 Measurements of the unknown samples

Start the measurements of the unknown samples.

Measure the drift control sample solution (CRM 1) at least once for every five unknown sample solutions. Maximum drifts allowed are given in Table 5.

If unacceptable drifting occurs, reject the results concerned and restart 9.4.2 and 9.4.3 procedures.

At the end of each analysis CRM 2, CRM 3 and the drift control solution should be re-determined.

NOTE To achieve a better repeatability of the determinations of phosphorus, it is advisable to carry out the measurements by bracketing the samples solutions with the most suitable multi-elemental calibration solutions.

Table 5 — Drift survey

Element	Content range %	Maximum drift %
All	0,001 to 0,002	0,000 1
	0,002 to 0,005	0,000 2
	0,005 to 0,01	0,000 3
	0,01 to 0,02	0,000 5
	0,02 to 0,05	0,002
	0,05 to 0,1	0,003
	0,1 to 0,2	0,004
	0,2 to 0,5	0,008
	0,5 to 1,0	0,013
	1,0 to 2,0	0,02

10 Expression of results

The calibration curves are drawn from the measurements carried out either in the “ratio” or in “intensity” mode according to the concentrations of the various elements.

On the calibration curves, read the contents, expressed in percent (mass fraction) of the elements determined in the test sample.

11 Precision

Fifteen laboratories in nine European countries participated in an inter laboratory validation test programme under the auspices of ECISS/TC 102/WG 10, involving three determinations of nine elements at several levels (from 8 to 14 depending on the element and its corresponding scope).

NOTE 1 Acid soluble aluminium was also included in the scope of the method sent for the precision test. However, due to a lack of precision in the results produced during this precision test, the determination of acid soluble aluminium was removed from the scope of this method.

Each laboratory carried out two determinations 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. The third determination was carried out on a different day using the same apparatus with a different calibration.

The composition of the samples used is given in Annex C.

The results obtained were treated statistically in accordance with ISO 5725 and CEN/TR 10345: they are reported in Annex D (Table D.1 to Table D.8).

Other than the repeatability with respect to tin, the data obtained showed logarithmic relationships between the contents of the different elements listed in the scope of this method and the corresponding repeatability (r) and reproducibility parameters (R_w and R). The corresponding graphical representations are shown in Annex E.

The repeatability limit (r) and reproducibility limits (R_w and R) of the test results are summarised in Table 6 to Table 12.

Table 6 — Silicon — Repeatability limit and reproducibility limits

Silicon content	Repeatability limit	Reproducibility limits	
% (mass fraction)	r	R_w	R
0,02	0,001 6	0,001 7	0,008 6
0,05	0,002 9	0,003 2	0,013 1
0,1	0,004 6	0,005 2	0,018 1
0,2	0,007 2	0,008 3	0,024 9
0,45	0,012 0	0,014 3	0,036 3

Table 7 — Manganese — Repeatability limit and reproducibility limits

Manganese content	Repeatability limit	Reproducibility limits	
% (mass fraction)	r	R_w	R
0,005	0,000 4	0,000 6	0,000 8
0,01	0,000 7	0,001 0	0,001 5
0,02	0,001 2	0,001 6	0,002 5
0,05	0,002 3	0,003 3	0,005 2
0,1	0,003 8	0,005 6	0,009 1
0,2	0,006 4	0,009 5	0,015 7
0,5	0,012 4	0,019 0	0,032 4
1,0	0,021	0,032	0,056
1,4	0,026	0,042	0,073

Table 8 — Phosphorus — Repeatability limit and reproducibility limits

Phosphorus content	Repeatability limit	Reproducibility limits	
% (mass fraction)	r	R_w	R
0,005	0,000 9	0,001 4	0,002 6
0,01	0,001 3	0,001 9	0,003 2
0,02	0,002 0	0,002 5	0,003 8
0,05	0,003 6	0,003 8	0,004 9
0,1	0,005 5	0,005 2	0,005 9

Table 9 — Copper — Repeatability limit and reproducibility limits

Copper content % (mass fraction)	Repeatability limit *r*	Reproducibility limits	
		R_w	R
0,005	0,000 3	0,000 4	0,000 9
0,01	0,000 5	0,000 7	0,001 4
0,02	0,000 8	0,001 2	0,002 2
0,05	0,001 7	0,002 5	0,004 1
0,1	0,002 9	0,004 3	0,006 5
0,2	0,005 1	0,007 6	0,010 4
0,5	0,010 6	0,016 1	0,019 3
0,6	0,012	0,019	0,022

Table 10 — Nickel — Repeatability limit and reproducibility limits

Nickel content % (mass fraction)	Repeatability limit *r*	Reproducibility limits	
		R_w	R
0,01	0,000 6	0,000 9	0,001 8
0,02	0,000 9	0,001 5	0,002 9
0,05	0,001 8	0,003 0	0,005 4
0,1	0,003 1	0,005 0	0,008 7
0,2	0,005 1	0,008 4	0,013 9
0,5	0,010 0	0,016 4	0,025 9
1,0	0,017	0,027	0,041
2,0	0,028	0,045	0,066

Table 11 — Chromium — Repeatability limit and reproducibility limits

Chromium content % (mass fraction)	Repeatability limit *r*	Reproducibility limits	
		R_w	R
0,01	0,000 7	0,001 5	0,002 7
0,02	0,001 0	0,002 4	0,004 0
0,05	0,001 9	0,004 2	0,006 7
0,1	0,002 9	0,006 5	0,009 8
0,2	0,004 6	0,010 0	0,014 4
0,5	0,008 2	0,017 8	0,024 0
0,9	0,012	0,026	0,033

Table 12 — Molybdenum — Repeatability limit and reproducibility limits

Molybdenum content % (mass fraction)	Repeatability limit r	Reproducibility limits R_w	 R
0,005	0,000 8	0,000 8	0,001 8
0,01	0,001 2	0,001 3	0,002 6
0,02	0,001 7	0,001 9	0,003 8
0,05	0,002 8	0,003 4	0,006 2
0,1	0,004 1	0,005 1	0,009 0
0,2	0,005 9	0,007 9	0,013 0
0,5	0,009 5	0,013 8	0,021 2
0,6	0,014	0,016	0,023

NOTE 2 Tin (repeatability limit and reproducibility limits) - For this element, only three samples were available for the validation of the method in the range 0,01 % to 0,1 % which is insufficient to assess the correlation between the content and the precision parameters. Therefore, only the experimental precision data reported in Table D.8 (see Annex D) apply.

12 Test report

The test report shall contain the following information:

a) identification of the test sample;

b) method used;

c) results;

d) any unusual characteristics noted during the determination;

e) any operation not included in this European Standard or in the document to which reference is made or regarded as optional;

f) date of the test and/or date of preparation or signature of the test report;

g) signature of the responsible person.

Annex A
(informative)

Plasma optical emission spectrometer — Suggested performance criteria to be checked

A.1 Practical resolution of the sequential spectrometer

The resolution of a spectrometer can be defined as the wavelength difference, $d\lambda$, between two lines which can still just be observed separately. In practice, the parameter FWHM (Full Width at Half Maximum) is used as a resolution measure.

Ideally, the resolution should be of the same order as the physical line width in plasma emission spectra, i.e. 2 pm to 5 pm (1 pm = 10^{-12} m). In practice, however, the observed width of the emission lines and, consequently, the resolution will often be determined by the bandwidth (r) of the spectrometer being used. As long as broadening resulting from aberrations can be neglected, this bandwidth is given by:

$$r = \text{FWHM} = (d\lambda/d\text{x})\ (w_\text{i} + w_\text{u})\ /2 \tag{A.1}$$

where

w_i and w_u are the widths of the entrance slit and exit slit respectively; and

$d\lambda/d\text{x}$ is the reciprocal linear dispersion which is given by:

$d\lambda/d\text{x} = d(\cos\beta)/\text{n}L$

where

L is the focal length of the spectrometer;

n is the order number;

d is the reciprocal of the groove density in the grating;

β is the diffraction angle.

Normally, commercial spectrometers present resolutions in the range of (4 to 30) pm. A good resolution is of great importance to cope with the frequent spectral interferences, which occur in inductively coupled plasma optical emission spectrometry. Since a line with a wavelength in the second order will have the same diffraction angle β as a line with a wavelength 2λ in the first order, a spectrometer should either have an order sorting possibility or an optical filter to avoid an order overlap.

A.2 Short and long term stability

The evaluation of the short-term stability consists on the calculation of the repeatability standard deviation of a series of measurements carried out with the spectrometer.

For each analyte, a series of ten consecutive intensity measurements of its highest multi-element calibration solution is carried out using the typical integration time for the system. The average I_avrg and the standard deviation S_I of the ten measurements are calculated in addition to the relative standard deviation RSD_I, according to the formula:

$$RSD_I = (S_I/I_{avrg}) \times 100 \text{ (in \%)} \qquad (A.2)$$

In inductively coupled plasma optical emission spectrometry, for solutions with concentrations of at least twice the background-equivalent concentration (BEC), RSD_I-values between 0,3 % and 1,0 % are generally accepted. Multi-elemental calibration solutions may be used for measurement at various analytical lines present in simultaneous optics.

Long-term stability assessment is a measurement of the instrument drift. This is only required if the spectrometer is set up to work for long intervals of time. It consists of carrying out the same short-term stability tests at specific intervals of time, 15 min to 1 h, and plotting the deviation of the average found for every short term test against time. Deviations of more than 2 % per hour should not be accepted. In case the instrument is not able to perform better, the control calibration solution should be measured more often during the analysis and the mean results of the test sample solutions should be recalculated by interpolation between two consecutive control calibration solutions.

The short and long-term stability data summarised in Table A.1 were obtained during the inter laboratory test program.

Table A.1 — Typical short and long term stability data

Element	Short term stability (%)	Long term stability (%)
Si	0,13 to 1,9	0,20 to 3,0
Mn	0,10 to 1,3	0,42 to 2,9
P	0,22 to 2,6	0,35 to 2,8
Cu	0,16 to 1,4	0,30 to 3,3
Ni	0,10 to 1,7	0,25 to 4,0
Cr	0,15 to 1,5	0,64 to 3,4
Mo	0,08 to 1,6	0,53 to 3,9
Sn	0,40 to 2,1	0,89 to 6,7

A.3 Evaluating the background equivalent concentration

The background equivalent concentration (BEC) is used as an evaluation of the instrument sensitivity. Since the analyte signal has usually a relatively high background, its correction by the background intensity is recommended. It is therefore calculated by using Formula (A.3):

$$BEC = (I_{BG} / I_{net}) \text{ x } C_{Analyte} \qquad (A.3)$$

where

I_{BG} is the intensity of the background;

I_{net} is the intensity of the analyte (overall intensity minus intensity of the background);

$C_{Analyte}$ is the concentration of analyte that yields I_{net}.

The background equivalent concentration values for the elements to be analysed can be found in wavelength tables (usually part of the instrument software). The background equivalent concentration is the better the smaller its numerical value is.

The background equivalent concentration data summarised in Table A.2 were obtained during the inter laboratory test program.

Table A.2 — Typical background equivalent concentration data

Element	Background equivalent concentration (mg/l)
Si	0,028 to 3,0
Mn	0,002 to 2,0
P	0,020 to 1,7
Cu	0,015 to 1,0
Ni	0,013 to 5,0
Cr	0,007 to 2,0
Mo	0,004 to 1,0
Sn	0,011 to 1,0

A.4 Evaluating the limit of detection

A.4.1 General

Two procedures may be followed, as described in A.4.2 and A.4.3.

The limit of detection data summarised in Table A.3 were obtained during the inter laboratory test program.

Table A.3 — Typical limit of detection data

Element	Limit of detection (mg/l)
Si	0,000 3 to 0,51
Mn	0,000 04 to 0,11
P	0,000 4 to 0,44
Cu	0,000 1 to 0,10
Ni	0,000 2 to 0,16
Cr	0,000 1 to 0,28
Mo	0,000 3 to 0,12
Sn	0,000 04 to 0,06

A.4.2 1st procedure

To an iron base solution, prepared as specified in 8.2, add the quantities of the analyte under concern in order to obtain solutions with concentration levels of 0,5, 1,0, 1,5, 2,0, 3,0 and 5,0 times the estimated limit of detection[2]. The other matrix components are then added. The quantity of each corresponds to the related upper limit of the scope.

All solutions are measured at least ten times (using the appropriate number of replicates).

The RSDs obtained are plotted against concentration and the graph obtained is used to read off the limit of detection.

This limit is the concentration at which the RSD is 33 %.

The limit of quantification is the concentration at which the RSD is 10 %.

A.4.3 2nd procedure

Operate as follows:

- For each element, measure 10 times under repeatability conditions, the intensity or the ratioed intensity of the "blank solution" and calculate the corresponding average (I_0) and standard deviation (σ_0).
- Then, for each element, measure 10 times under repeatability conditions, the intensity or the ratioed intensity of the lowest concentration (C_x) standard solution (lowest limit of each proposed range of content) and calculate each corresponding average (I_x).
- Taking into account the statistical risks α and β each of them at the 95 % level (4,65), the limit of detection (C_{lim}) is calculated according to the formula:

$$C_{lim} = \frac{4{,}65 \times \sigma_0 \times C_x}{I_x - I_0} \tag{A.4}$$

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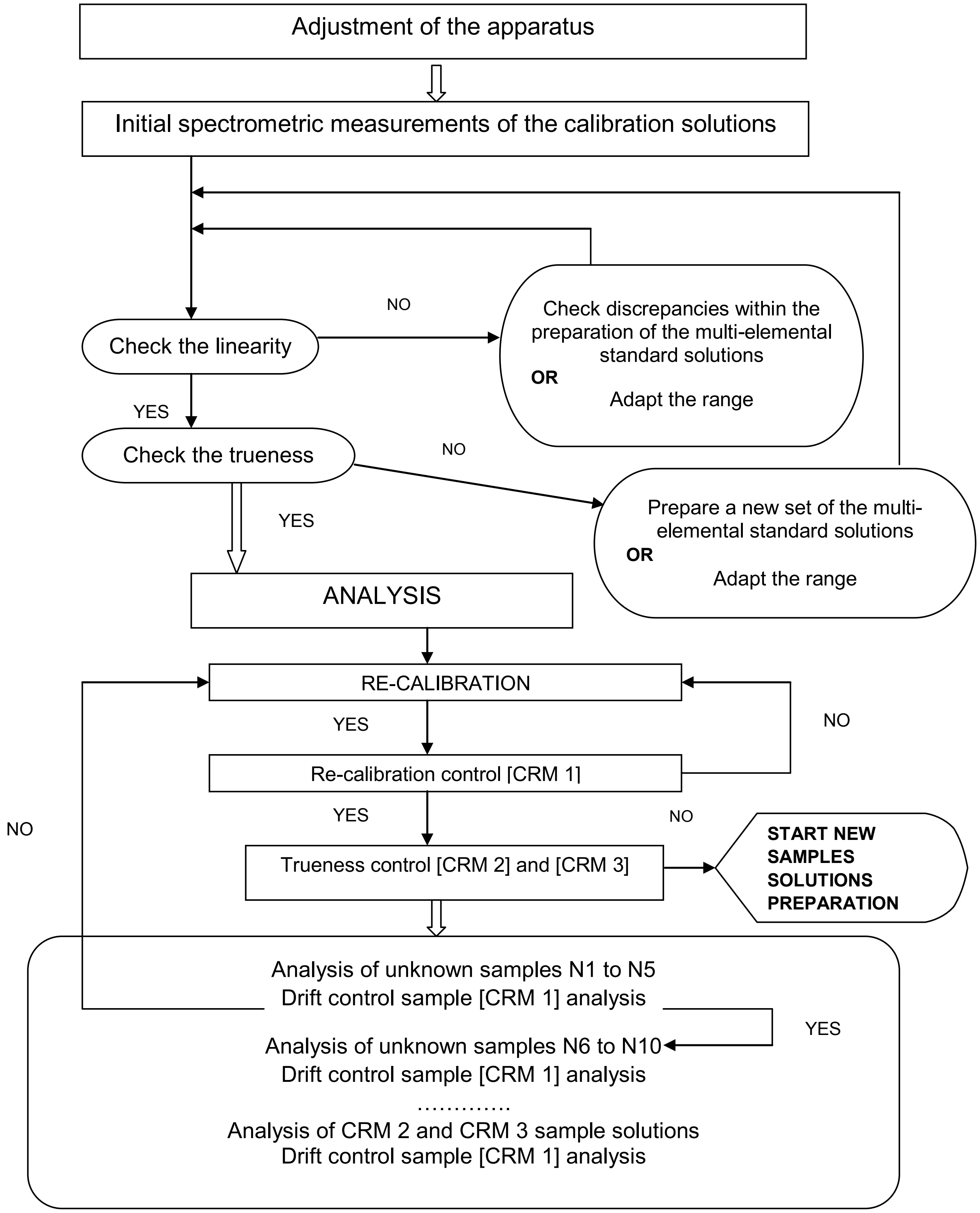
[2] The "estimated limit of detection" can be assessed through the data provided by the manufacturer or through the method described in A.4.3.

Annex B
(normative)

Synoptic of the operations related to Clause 9



Annex C
(informative)

Composition of the test samples used for the validation precision test

The composition of the test samples used are listed in Table C.1. Elements and/or contents reported in grey cells were out of the scope of the validation precision test.

Table C.1 — Composition of the test samples used for the validation precision test

Sample label	C	Si	Mn	S	P	Cu	Ni	Cr	Mo	Sn	$Al_{(tot)}$	Ti	V	Co	Others
1 [ECRM 035-2]	1,28	0,22	0,31	0,011	0,004	0,009	0,020	0,010	0,006		0,019	0,003			As: 0,002
2 [ECRM 183-1]	0,083	0,42	0,35	0,031	0,089	0,45	0,073	0,67			0,027				As: 0,001
3 [ECRM 088-2]		0,005	0,081	0,007	0,005	0,016	0,028	0,024	0,003						
4 [ECRM 097-1]			0,006	0,002	0,002	0,002	0,003	0,002						0,004	As: 0,005; B: 0,0003
5 [IRM 41]	0,327	0,253	0,587	0,003	0,009	0,094	1,57	0,828	0,032	0,009 5	< 0,005	< 0,002	< 0,010	0,045	
6 [ECRM 193-1]	0,14	0,40	0,97	0,009	0,006	0,60	1,18	0,18	0,35	0,003 5	0,026			0,007	As: 0,006; Nb: 0,02
7 [ECRM 195-1]	0,76	0,47	0,57	0,012	0,016	0,035	0,33	1,57	0,77	0,002 0	0,025		0,31		Ca: 0,002; Pb: 0,001; Zn: 0,005
8 [BCS 111]	0,026	0,025	0,16	0,005	0,003	0,017	0,039	0,020	0,000 8	0,001 5	0,035	0,000 4	0,000 9	0,014	As: 0,002
9 [BCS 453/1]	0,16	0,34	1,38	0,026	0,044	0,10	0,11	0,26	0,081	0,022	0,005	0,073			As: 0,05; W: 0,3
10 [BCS 452/1]	0,32	0,06	1,30	0,017	0,035	0,22	0,19	0,067	0,054	0,094		0,031			As: 0,015; W 0,05
11 [BCS 402/2]	1,31	0,11	0,23	0,014	0,016	0,30	0,81	0,65	0,14		0,161		0,19		
12 [IRM HOG]		0,005	0,20		0,005	0,02	1,9	0,02	0,57	0,002 5	0,005				

Annex D
(informative)

Detailed results obtained from the validation precision test

Table D.1 — Silicon

	1	2	5	6	8	9	10	11
Mean, %	0,216 9	0,423 7	0,256 6	0,403 7	0,023 6	0,342 8	0,053 2	0,105 7
σ (r), %	0,002 8	0,005 6	0,003 0	0,004 3	0,000 7	0,002 9	0,001 3	0,001 1
σ (R_w), %	0,006 4	0,004 5	0,002 5	0,004 2	0,000 8	0,005 5	0,001 2	0,001 1
σ (R), %	0,008 7	0,015 9	0,008 9	0,012 1	0,004 2	0,012 3	0,004 2	0,005 3
r, %	0,007 9	0,015 5	0,008 5	0,011 9	0,002 0	0,008 1	0,003 7	0,003 0
R_w, %	0,017 9	0,012 7	0,006 9	0,011 9	0,002 2	0,015 3	0,003 5	0,003 0
R, %	0,022 4	0,044 6	0,024 9	0,034 0	0,011 7	0,034 6	0,011 8	0,014 8
CV (R)	4,02	3,76	3,47	3,01	**17,61**	3,60	7,94	5,00
Aim CV (R)	2,51	1,99	2,37	2,02	5,41	2,14	4,08	3,22
Max CV (R)	5,51	4,37	5,20	4,45	11,89	4,71	8,98	7,07

Table D.2 — Manganese

	1	2	3	4	5	6	8	9	10	11	12
Mean, %	0,303 6	0,355 9	0,081 0	0,006 39	0,573 6	0,982 1	0,155 7	1,386 2	1,324 8	0,227 7	0,209 7
σ (r), %	0,00 2 8	0,002 3	0,002 0	0,000 21	0,006 4	0,006 9	0,001 1	0,012 2	0,011 0	0,001 6	0,002 8
σ (R_w), %	0,004 1	0,003 9	0,001 7	0,000 32	0,009 9	0,010 2	0,002 2	0,014 0	0,025 5	0,003 2	0,003 1
σ (R), %	0,007 6	0,008 0	0,005 3	0,000 30	0,013 0	0,017 2	0,004 0	0,021 9	0,032 2	0,005 4	0,005 5
r, %	0,007 9	0,006 5	0,005 7	0,000 57	0,018 0	0,019 2	0,002 9	0,034 2	0,030 8	0,004 5	0,007 8
R_w, %	0,011 4	0,010 9	0,004 6	0,000 90	0,027 8	0,028 6	0,006 2	0,039 3	0,071 4	0,008 9	0,008 6
R, %	0,021 3	0,022 5	0,014 9	0,000 85	0,036 5	0,048 2	0,011 1	0,061 2	0,093 0	0,015 2	0,015 3
CV (R)	2,51	2,26	6,57	4,75	2,27	1,72	2,54	1,58	2,51	2,39	2,60
Aim CV (R)	2,23	2,11	3,53	8,51	1,79	1,49	2,81	1,32	1,34	2,47	2,54
Max CV (R)	4,91	4,64	7,76	18,71	3,94	3,27	6,19	2,90	2,95	5,42	5,58

Table D.3 — Phosphorus

	1	**2**	**3**	**5**	**6**	**8**	**9**	**10**	**11**	**12**
Mean, %	0,003 44	0,088 3	0,004 52	0,009 39	0,006 24	0,003 77	0,041 1	0,033 8	0,015 5	0,004 26
σ (r), %	0,000 64	0,001 9	0,000 33	0,000 58	0,000 48	0,000 69	0,001 0	0,000 9	0,000 6	0,000 17
σ (R_w), %	0,000 51	0,001 9	0,000 58	0,000 59	0,000 67	0,000 51	0,001 1	0,001 1	0,000 9	0,000 32
σ (R), %	0,000 57	0,002 3	0,000 95	0,001 05	0,000 86	0,000 63	0,001 8	0,001 3	0,001 4	0,001 04
r, %	0,001 78	0,005 4	0,000 93	0,001 63	0,001 34	0,001 92	0,002 7	0,002 6	0,001 7	0,000 48
R_w, %	0,001 42	0,005 2	0,001 63	0,001 65	0,001 87	0,001 43	0,003 1	0,003 0	0,002 7	0,000 89
R, %	0,001 59	0,006 3	0,002 67	0,002 94	0,002 41	0,001 76	0,004 9	0,003 5	0,003 8	0,002 92
CV (R)	16,49	2,56	**21,08**	11,18	13,79	16,65	4,29	3,73	8,78	**24,51**
Aim CV (R)	10,56	3,43	9,60	7,45	8,58	10,22	4,47	4,78	6,26	9,80
Max CV (R)	23,20	7,53	21,10	16,37	18,66	22,47	9,82	10,50	13,76	21,54

Table D.4 — Copper

	1	2	3	5	6	8	9	10	11	12
Mean, %	0,008 02	0,444 3	0,016 3	0,092 9	0,602 2	0,016 9	0,097 9	0,217 0	0,304 8	0,024 3
σ (r), %	0,000 11	0,002 5	0,000 3	0,000 6	0,005 4	0,000 3	0,001 0	0,002 5	0,002 8	0,000 4
σ (R_w), %	0,000 29	0,005 5	0,000 3	0,001 4	0,007 9	0,000 4	0,001 0	0,003 1	0,004 0	0,000 4
σ (R), %	0,000 52	0,007 4	0,000 7	0,001 9	0,008 4	0,000 7	0,001 7	0,003 7	0,005 5	0,000 9
r, %	0,000 30	0,006 9	0,000 7	0,001 8	0,015 0	0,001 0	0,002 8	0,006 9	0,007 8	0,001 1
R_w, %	0,000 82	0,015 3	0,000 9	0,003 9	0,022 2	0,001 1	0,002 9	0,008 8	0,011 3	0,001 1
R, %	0,001 47	0,020 7	0,001 9	0,005 4	0,023 6	0,002 0	0,004 7	0,010 4	0,015 4	0,002 4
CV (R)	6,52	1,66	4,05	2,08	1,40	4,22	1,71	1,72	1,81	3,59
Aim CV (R)	7,87	1,96	6,15	3,37	1,76	6,07	3,31	2,51	2,23	5,36
Max CV (R)	17,29	4,30	13,51	7,40	3,87	13,34	7,27	5,51	4,90	11,77

Table D.5 — Nickel

	1	2	3	5	6	8	9	10	11	12
Mean, %	0,017 6	0,071 7	0,026 8	1,551 3	1,184 4	0,038 6	0,106 3	0,191 0	0,817 8	1,936 0
σ (r), %	0,000 5	0,000 9	0,000 5	0,007 5	0,006 1	0,000 3	0,001 0	0,001 4	0,007 6	0,010 7
σ (R_w), %	0,000 7	0,001 0	0,000 5	0,013 0	0,011 0	0,00 08	0,002 1	0,003 6	0,008 3	0,016 3
σ (R), %	0,001 5	0,001 6	0,001 5	0,016 9	0,015 5	0,001 3	0,002 8	0,005 1	0,013 6	0,033 2
r, %	0,001 5	0,002 5	0,001 3	0,020 9	0,017 0	0,000 8	0,002 8	0,003 8	0,021 4	0,029 9
R_w, %	0,002 0	0,002 8	0,001 5	0,036 3	0,030 8	0,002 4	0,005 8	0,010 1	0,023 2	0,045 5
R, %	0,004 1	0,004 3	0,004 1	0,047 3	0,043 3	0,003 7	0,007 9	0,014 4	0,038 2	0,093 0
CV (R)	8,37	2,18	5,51	1,09	1,30	3,39	2,66	2,69	1,67	1,71
Aim CV (R)	6,00	3,68	5,18	1,27	1,39	4,56	3,21	2,62	1,58	1,17
Max CV (R)	13,18	8,09	11,38	2,79	3,06	10,03	7,06	5,76	3,48	2,58

Table D.6 — Chromium

	1	2	3	5	6	8	9	10	11	12
Mean, %	0,009 65	0,675 0	0,023 7	0,835 3	0,183 2	0,019 3	0,259 0	0,067 6	0,653 5	0,023 8
σ (r), %	0,000 13	0,004 2	0,000 9	0,002 5	0,001 0	0,000 4	0,001 8	0,000 8	0,005 9	0,000 4
σ (R_w), %	0,000 34	0,012 9	0,001 4	0,008 2	0,003 1	0,000 8	0,004 5	0,000 9	0,005 3	0,002 1
σ (R), %	0,000 65	0,012 8	0,002 1	0,011 8	0,002 9	0,001 1	0,005 6	0,001 7	0,010 9	0,004 5
r, %	0,000 37	0,011 8	0,002 4	0,007 1	0,002 9	0,001 1	0,005 0	0,002 1	0,016 6	0,001 2
R_w, %	0,000 95	0,036 1	0,003 9	0,022 9	0,008 7	0,002 2	0,012 5	0,002 5	0,014 9	0,005 7
R, %	0,001 82	0,036 0	0,005 8	0,033 2	0,008 3	0,003 0	0,015 8	0,004 9	0,030 6	0,012 6
CV (R)	6,74	1,90	8,70	1,42	1,61	5,46	2,18	2,58	1,67	**18,96**
Aim CV (R)	7,38	1,96	5,40	1,57	2,66	5,80	2,36	3,76	1,71	5,39
Max CV (R)	16,22	3,72	11,87	3,46	5,85	12,75	5,19	8,26	3,76	11,86

Table D.7 — Molybdenum

	1	2	5	6	9	10	11	12
Mean, %	0,004 94	0,016 8	0,026 8	0,350 0	0,076 6	0,053 3	0,141 3	0,571 3
σ (r), %	0,000 43	0,000 5	0,000 5	0,003 8	0,000 9	0,000 4	0,001 2	0,005 6
σ (R_w), %	0,000 40	0,000 8	0,000 5	0,003 2	0,001 0	0,001 0	0,003 1	0,008 2
σ (R), %	0,000 83	0,001 3	0,001 6	0,006 8	0,002 0	0,001 6	0,004 2	0,010 4
r, %	0,001 21	0,001 4	0,001 3	0,010 6	0,002 5	0,001 3	0,003 3	0,015 7
R_w, %	0,001 12	0,002 2	0,001 5	0,009 1	0,002 9	0,002 8	0,008 6	0,023 0
R, %	0,002 32	0,003 8	0,004 5	0,019 0	0,005 6	0,004 4	0,011 6	0,029 0
CV (R)	16,79	8,00	5,95	1,94	2,61	2,98	2,94	1,81
Aim CV (R)	9,31	6,09	5,18	2,13	3,60	4,08	2,91	1,79
Max CV (R)	20,45	13,39	11,38	4,67	7,91	8,97	6,40	3,94

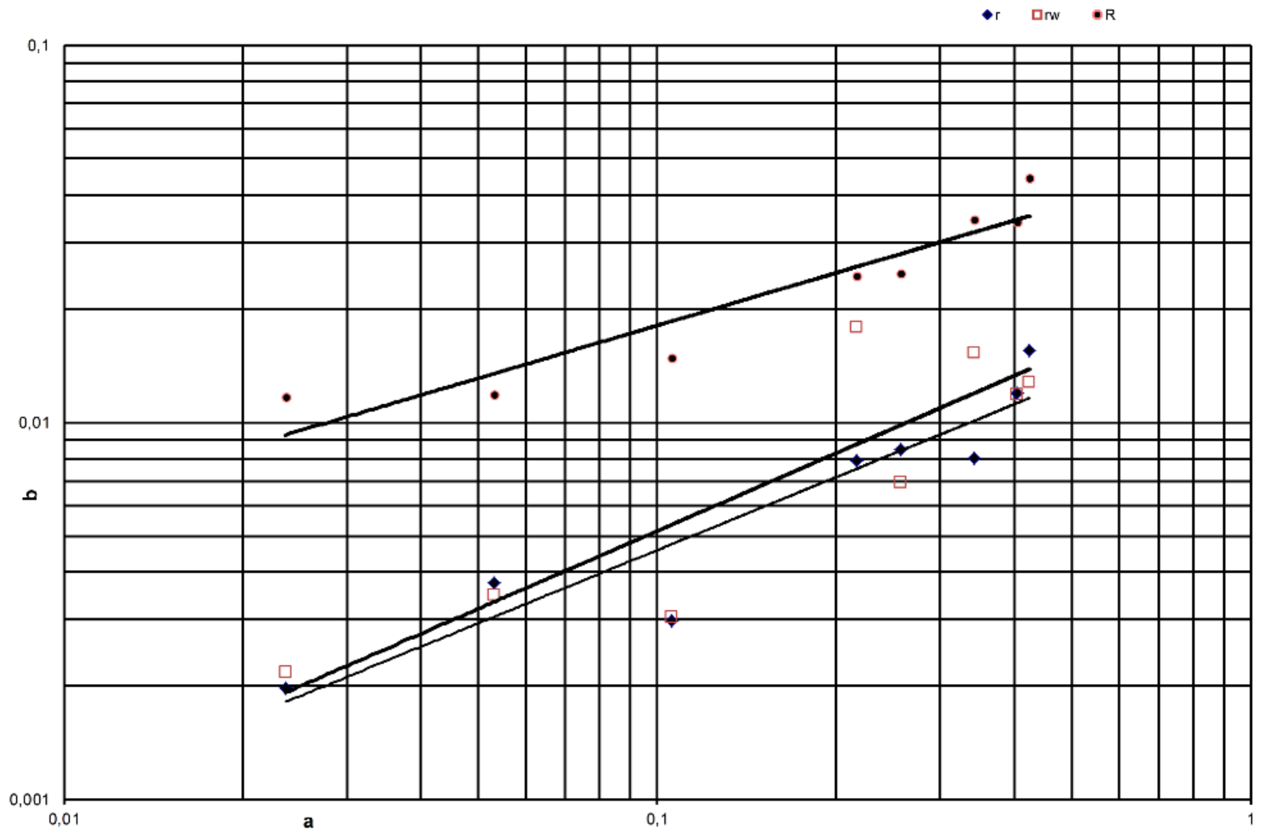
Table D.8 — Tin

	2	**3**	**5**	**6**	**8**	**9**	**10**	**12**
Mean, %	0,013 4	0,002 64	0,008 63	0,003 32	0,001 54	0,021 2	0,093 8	0,002 37
σ (r), %	0,000 1	0,000 11	0,000 39	0,000 27	0,000 30	0,000 3	0,001 0	0,000 32
σ (R_w), %	0,000 5	0,000 18	0,000 30	0,000 30	0,000 27	0,000 5	0,001 5	0,000 27
σ (R), %	0,000 7	0,000 32	0,000 55	0,000 47	0,000 40	0,000 9	0,002 6	0,000 54
r, %	0,000 3	0,000 31	0,001 08	0,000 74	0,000 84	0,000 8	0,002 7	0,000 90
R_w, %	0,001 5	0,000 52	0,000 84	0,000 83	0,000 76	0,001 5	0,004 2	0,000 77
R, %	0,002 0	0,000 89	0,001 53	0,001 32	0,001 12	0,002 4	0,007 2	0,001 50
CV (R)	5,41	12,00	6,35	14,22	25,89	4,06	2,74	22,61
Aim CV (R)	6,59	11,57	7,67	10,68	13,94	5,62	3,36	12,01
Max CV (R)	14,48	25,43	16,86	23,48	30,64	12,35	7,37	26,40

Annex E
(informative)

Graphical representation of the precision data

Figure E.1 to Figure E.7 show the logarithmic relationships between the content of each element (m) and the corresponding repeatability (*r*) and reproducibility parameters (R_w and *R*).



Key

a Si content % (m/m)

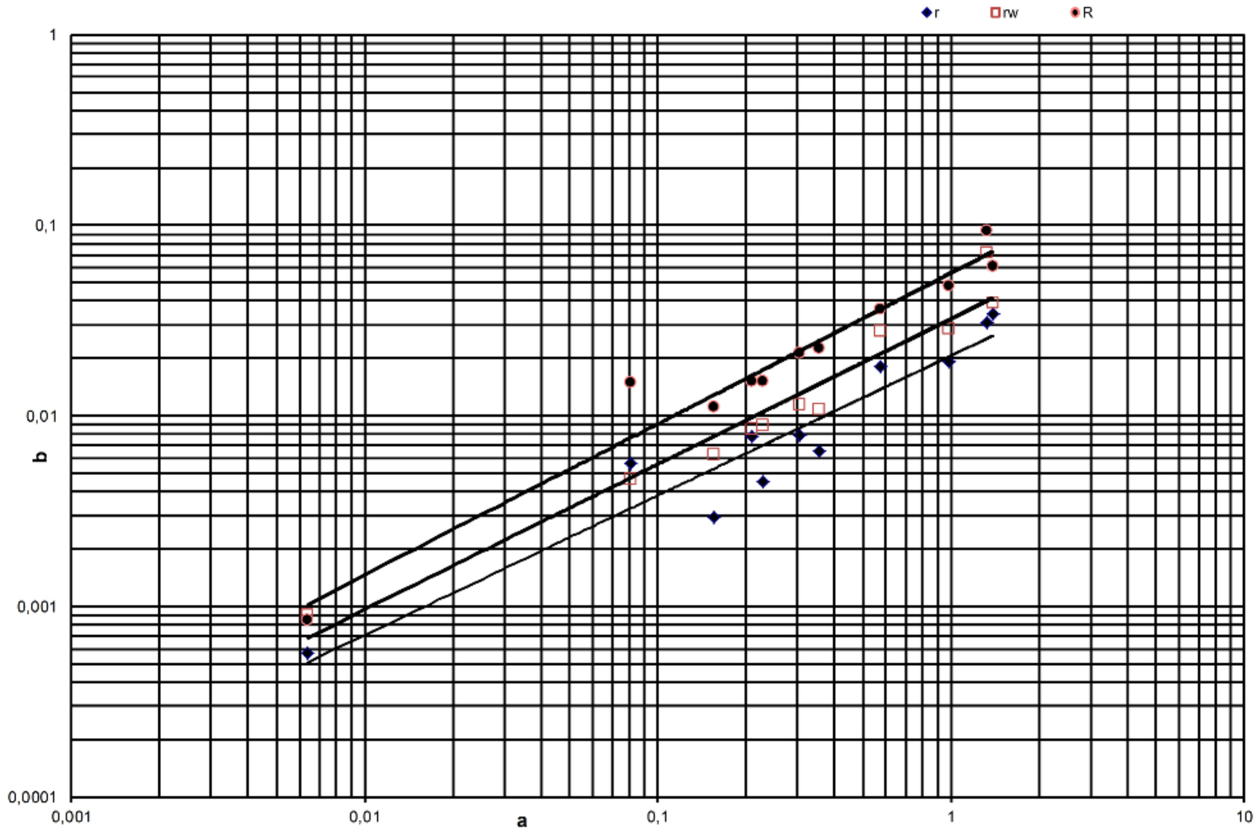
b Precision (%)

$\lg r = 0,642\,9 * \lg m - 1,696\,2$

$\lg R_w = 0,684\,3 * \lg m - 1,603\,8$

$\lg R = 0,463\,4 * \lg m - 1,279\,8$

Figure E.1 — Silicon



Key

a Mn content % (m/m)

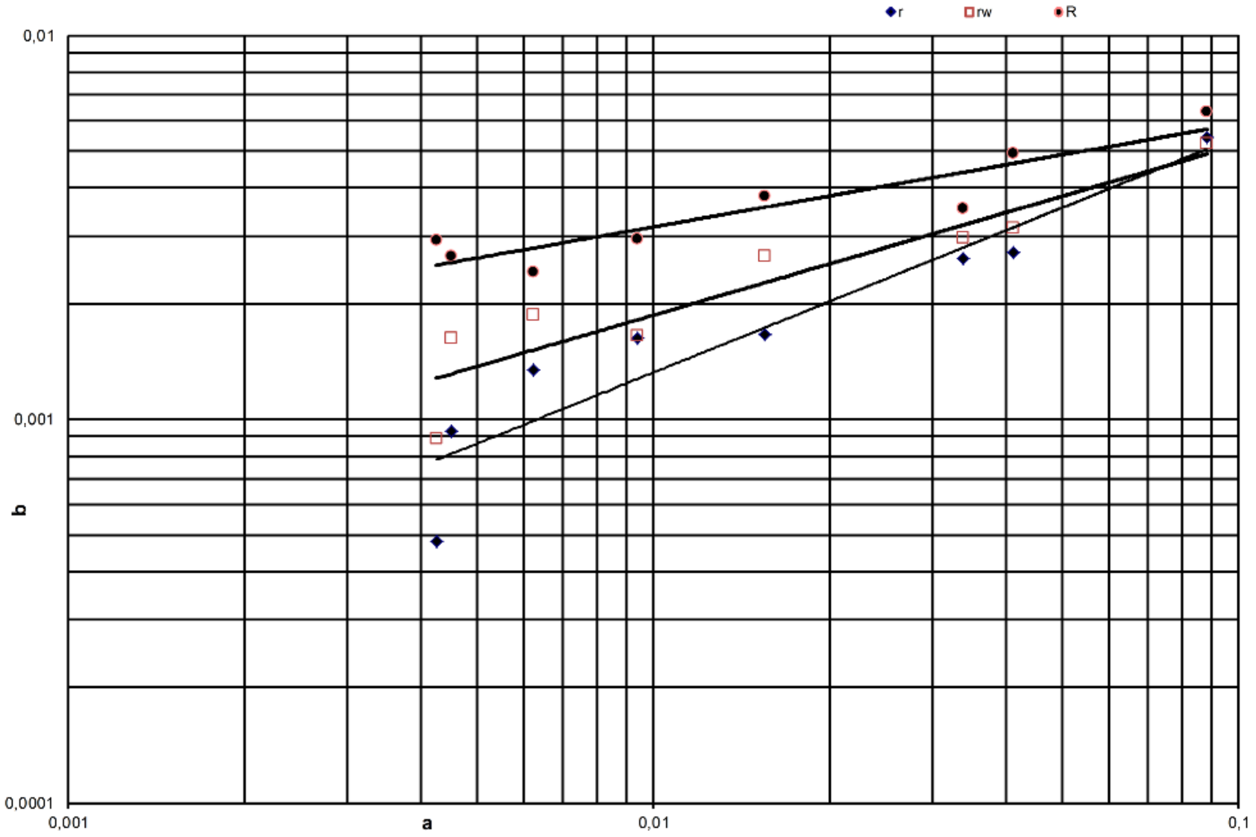
b Precision (%)

lg r = 0,732 7 * lg m – 1,684 7

lg R_w = 0,762 3 * lg m – 1,491 2

lg R = 0,791 7 * lg m – 1,251 2

Figure E.2 — Manganese



Key

a P content % (m/m)

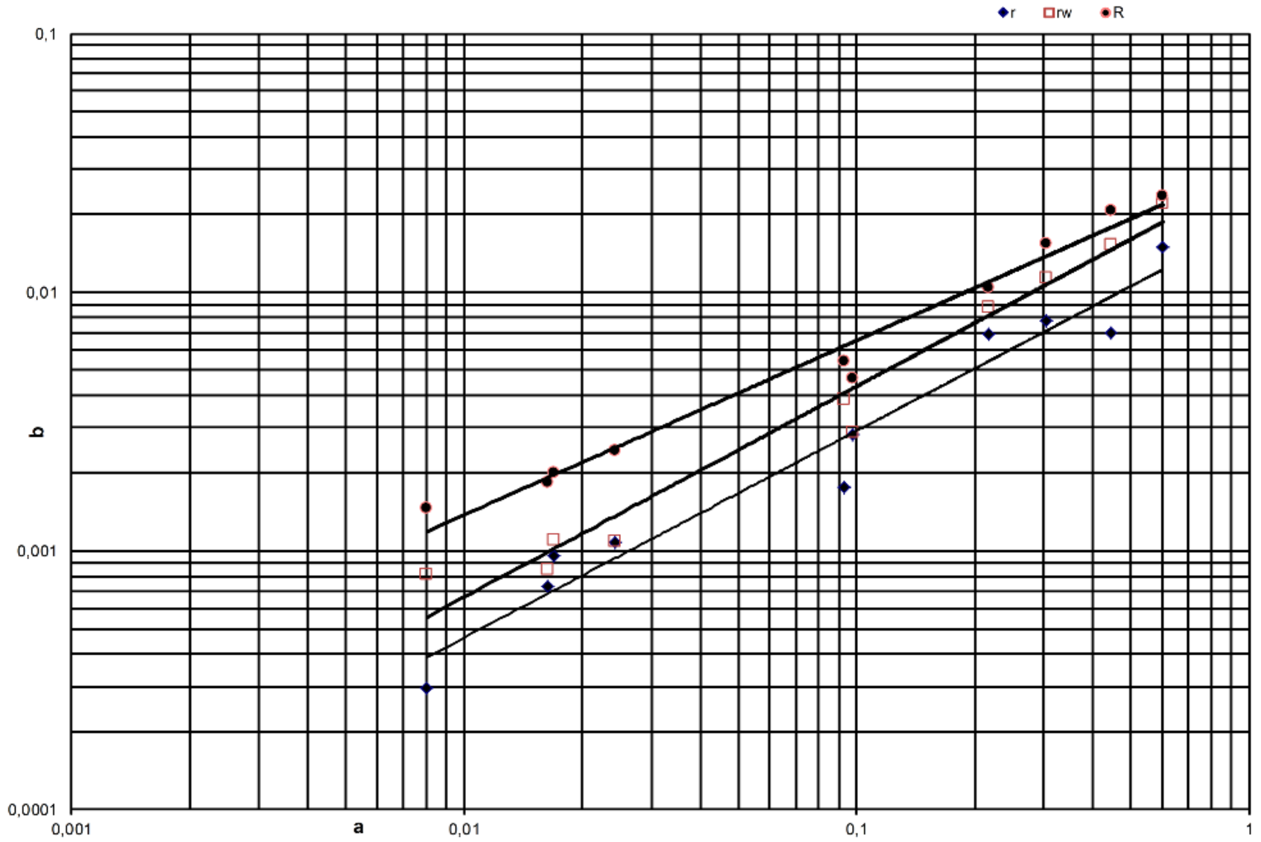
b Precision (%)

lg r = 0,614 9 * lg m – 1,648 5

lg R_w = 0,443 8 * lg m – 1,841 3

lg R = 0,268 5 * lg m – 1,961 8

Figure E.3 — Phosphorus



Key

a Cu content % (m/m)

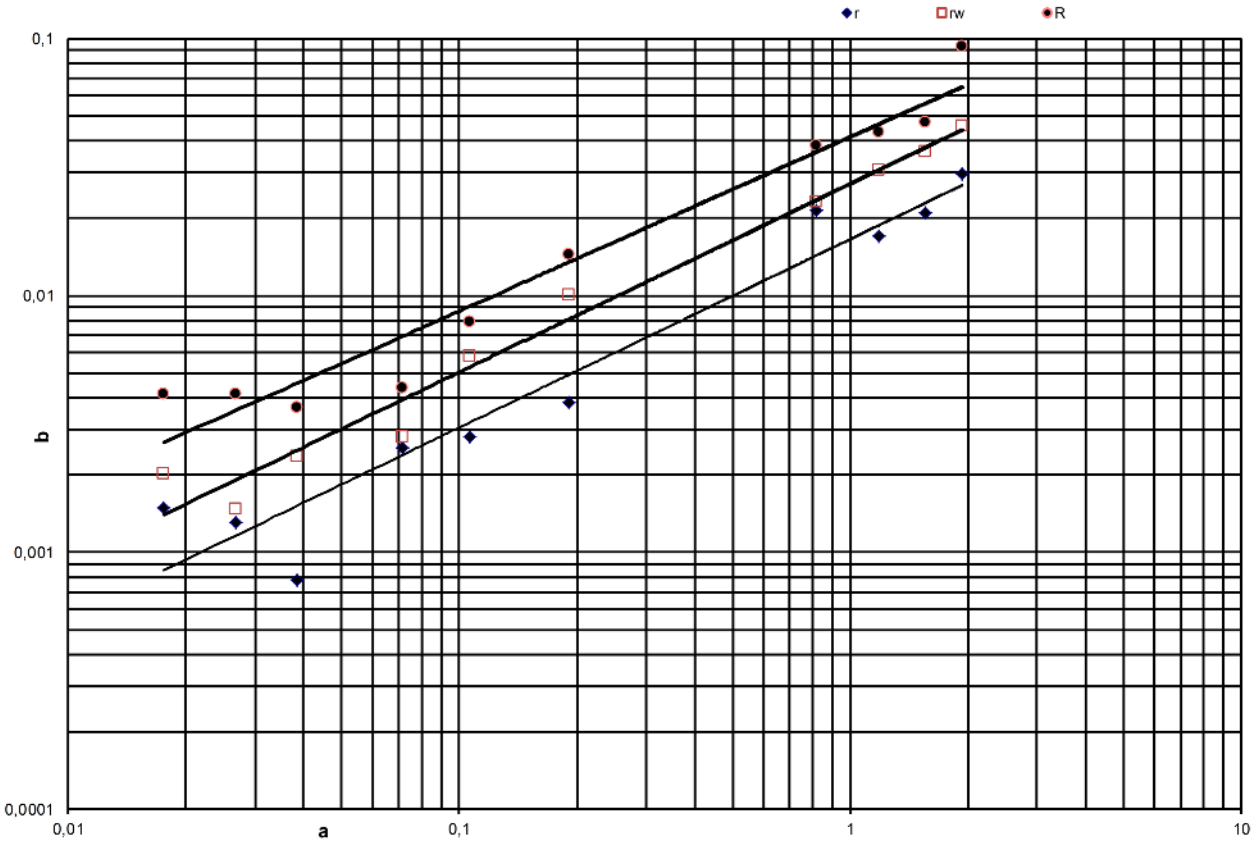
b Precision (%)

lg r = 0,800 3 * lg m – 1,735 2

lg R_w = 0,814 5 * lg m – 1,549 3

lg R = 0,674 2* lg m – 1,512 2

Figure E.4 — Copper



Key

a Ni content % (m/m)

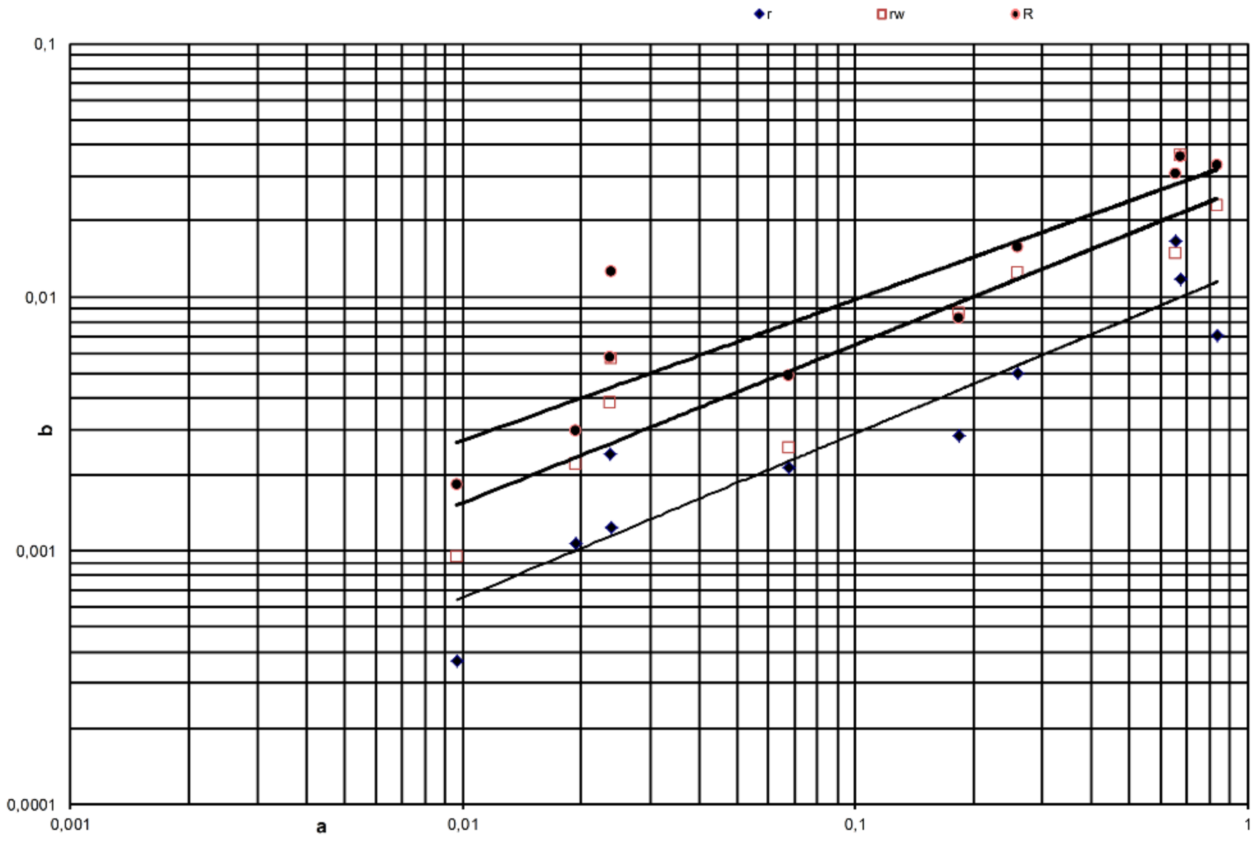
b Precision (%)

lg r = 0,733 6 * lg m – 1,780 5

lg R_w = 0,733 6 * lg m – 1,564 7

lg R = 0,677 7 * lg m – 1,382 5

Figure E.5 — Nickel



Key

a Cr content % (m/m)

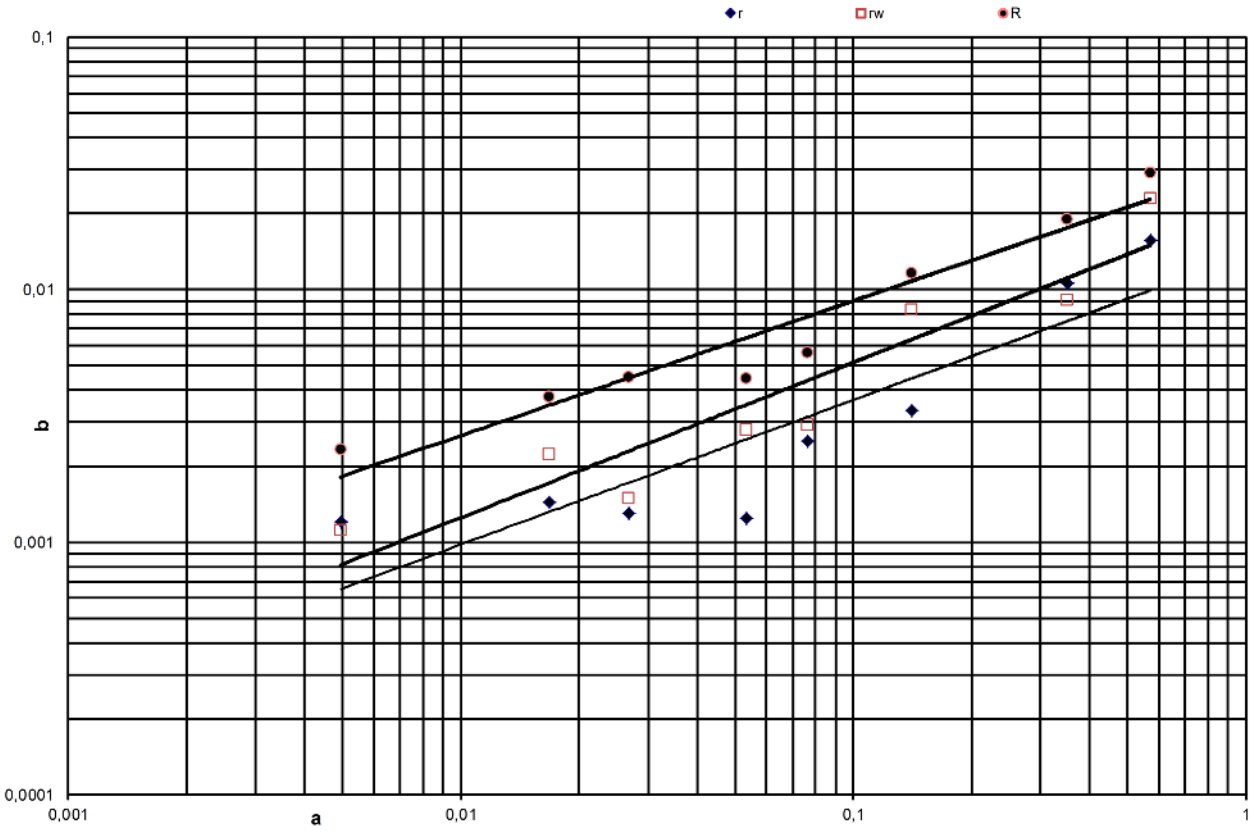
b Precision (%)

lg r = 0,647 7 * lg m – 1,889 0

lg R_w = 0,624 9 * lg m – 1,561 5

lg R = 0,556 4 * lg m – 1,452 7

Figure E.6 — Chromium



Key

a Mo content % (m/m)

b Precision (%)

lg r = 0,572 6 * lg m – 1,864 0

lg R_w = 0,613 5 * lg m – 1,.674 9

lg R = 0,532 3 * lg m – 1,512 5

Figure E.7 — Molybdenum

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