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Chemical analysis of ferrous materials — Inductively coupled plasma optical emission spectrometric analysis of unalloyed and low alloyed steels — Determination of Mn, P, Cu, Ni, Cr, Mo, V, Co, Al (total) and Sn [Routine method]

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National foreword

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Chemical analysis of ferrous materials - Inductively coupled plasma optical emission spectrometric analysis of unalloyed and low alloyed steels - Determination of Mn, P, Cu, Ni, Cr, Mo, V, Co, Al (total) and Sn [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 Mn, P, Cu, Ni, Cr, Mo, V, Co, Al (total) et Sn [Méthode de routine]

Chemische Analyse von Eisenwerkstoffen - Analyse von unlegierten und niedrig legierten Stählen mittels optischer Emissionsspektrometrie mit induktiv gekoppeltem Plasma - Bestimmung von Mn, P, Cu, Ni, Cr, Mo, V, Co, Al (gesamt) und Sn [Routineverfahren]

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Foreword

This document (EN 10351:2011) 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of an identical text or by endorsement, at the latest by September 2011, and conflicting national standards shall be withdrawn at the latest by September 2011.

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

Table 1 — Application ranges

Element	**Mass fraction %**	
	min.	max.
Mn	0,005	2,00
P	0,005	0,05
Cu	0,005	0,80
Ni	0,010	2,00
Cr	0,010	1,60
Mo	0,005	0,80
V	0,002	0,40
Co	0,002	0,10
Al (total)	0,020	0,30
Sn	0,001	0,10

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.

NOTE 1 The accuracy of the method is unsatisfactory for phosphorus contents from 0,05 to 0,1 %.

NOTE 2 The trueness of the method couldn't be checked for vanadium contents below 0,05 %.

NOTE 3 The precision of the method is unsatisfactory for aluminium (total) contents below 0,02 %.

2 Normative references

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

CEN/TR 10345:2008, *Guideline for statistical data treatment of inter laboratory tests for validation of analytical methods*

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

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

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

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

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

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

3 Principle

Dissolution of a test portion with nitric and hydrochloric acids. Filtration and ignition of the acid insoluble residue. Removal of silica with hydrofluoric acid. Fusion of the residue with a mixture of orthoboric acid and potassium carbonate, dissolution of the melt with acid and addition of this solution to the reserved filtrate.

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 Hydrofluoric acid, HF (ρ_{20} = 1,13 g/ml)

WARNING — Hydrofluoric acid is extremely irritating and corrosive to skin and mucous membranes producing severe skin burns which are slow to heal. In the case of contact with skin, wash well with water, apply a topical gel containing 2,5 % (mass fraction) calcium gluconate, and seek immediate medical treatment.

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

4.7 Sulphuric acid, solution 1 + 1

Add 25 ml of sulphuric acid (4.6) to 25 ml of water and allow it to cool.

4.8 Fusion reagent

4.8.1 Fusion mixture

Mix one part by mass of orthoboric acid, H_3BO_3 and one part of potassium carbonate anhydrous, K_2CO_3.

4.8.2 Fusion mixture, 100 g/l solution

In a suitable beaker, dissolve 25 g of the fusion mixture (4.8.1). Heat if necessary. After cooling, transfer the solution quantitatively into a 250 ml one-mark volumetric flask, dilute to the mark with water and mix well.

4.9 Aluminium, 1 g/l standard solution

Weigh (0,5 ± 0,001) g of aluminium (99,99 % purity) and transfer into a 400 ml beaker. Add 50 ml of hydrochloric acid solution (4.2) and heat gently until aluminium 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 Al.

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 Cobalt 1 g/l standard solution

Weigh (0,5 ± 0,001) g of cobalt (99,99 % purity) and transfer into a 250 ml beaker. Dissolve it in 5 ml of hydrochloric acid (4.1) and 5 ml of nitric acid (4.3). 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 Co.

4.12 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, 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.

4.13 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 (4.6). 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 minutes 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.

4.14 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.

4.15 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, 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.

4.16 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.

4.17 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.

4.18 Vanadium 1 g/l standard solution

Weigh (0,5 ± 0,001) g of vanadium (99,99 % purity) and transfer into a 250 ml beaker. Dissolve it in 30 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 V.

NOTE Standard solutions whose preparations are described under items 4.9 to 4.18 can be replaced by commercial available standard solutions, provided that they are supplied by a recognised producer and their traceability fully documented.

4.19 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 as Cd, Fe, Sc and Y were used for this purpose during the validation precision test of this method.

4.20 Pure iron

The purity of the iron selected shall be at least ten times better than the low limit of the scope of each element included in the present method.

5 Apparatus

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

5.1 Close texture filter paper and/or 0,45 µm cellulose nitrate filter

5.2 Filter funnel suitable for 0,45 µm filters

Two-pieces acid-resistant filter funnel with a support screen between the funnel body and stem, designated for the vacuum filtration of liquids. The stem of the filter is fitted with a ground glass cap stopper or a rubber stopper for insertion into an opening of the vacuum vessel.

5.3 Vacuum vessel

With an opening to allow the insertion of the stopper of the filter funnel stem.

5.4 Platinum crucibles and covers

5.5 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 steels.

7 Sample solution preparation

7.1 Test portion

Weigh, to the nearest 0,001 g, 1 g of the test sample.

7.2 Preparation of the test solution

7.2.1 Dissolution of the test portion

Transfer the test portion (7.1) into a 250 ml or 400 ml beaker.

Add 5 ml of nitric acid (4.3) and 20 ml of hydrochloric acid solution (4.2). Cover and heat gently until the attack reaction ceases. Heat at a temperature of about 95 °C, for about 5 minutes. Allow to cool.

Rinse the beaker cover and the walls of the beaker with water.

7.2.2 Filtration of the test solution

7.2.2.1 Including total aluminium determination

Place a 0,45 µm cellulose nitrate filter (5.1) on the support screen of a filter funnel (5.2). Moisten the filter with water and join the body and stem of the funnel. Insert the stopper of the filter funnel stem into a vacuum vessel (5.3). Apply vacuum gently to the vacuum vessel and filter the solution. Wash the funnel sides and residue with warm water several times.

Stop the vacuum gently.

Wipe the funnel sides with a close texture filter paper, then place the cellulose nitrate filter in this filter paper and fold them.

Transfer the folded filters into a platinum crucible (5.4) and cover with a suitable platinum cover.

Transfer the filtrate quantitatively into a 200 ml one-mark volumetric flask.

7.2.2.2 Excluding total aluminium determination

Filter the solution through a close texture filter paper and collect the filtrate into a 200 ml one-mark volumetric flask.

Wash the filter paper and residue with warm water several times and collect the washings in the volumetric flask.

Transfer the filter into a platinum crucible (5.4) and cover with a suitable platinum cover.

7.2.3 Treatment of the insoluble residue

Introduce the crucible in a COLD furnace, then switch it on in order to reach a temperature of about 900 °C. Allow to stand at 900 °C for about 15 min. Cool the crucible. Add into the crucible 0,5 to 1,0 ml of sulphuric acid solution (4.7) and 2 ml of hydrofluoric acid (4.5). Evaporate to dryness and cool.

Add 1,0 g of the fusion mixture (4.8.1). Fuse the content of the crucible in a muffle furnace at 1 000 °C for 15 min to 20 min. Cool the crucible and add 20 ml of hydrochloric acid solution (4.2) to the solidified melt. Heat gently, in order to dissolve the fusion products. Allow the crucible to cool and add this solution quantitatively to the filtrate in the 200 ml volumetric flask.

If an internal reference element is used add, with a calibrated pipette, 10 ml of the internal reference element solution (4.19).

NOTE 1 Depending on the instrument performances, the volume and/or the concentration of the internal reference element solution may be different.

Dilute to the mark with water and mix.

NOTE 2 Depending on the instrument performances, suitable dilutions of the sample solution and of the calibration solutions may be necessary.

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

Weigh the quantities of pure iron (4.20) shown in Table 2 and introduce them into each of a series of 250 ml or 400 ml beakers.

Add 20 ml of the hydrochloric acid solution (4.2) to each beaker. Cover with a watch glass and heat gently. When the attack reaction ceases, add 5 ml of nitric acid (4.3). Heat until nitrous fumes have been expelled.

Rinse the cover and the walls of the beaker with water and heat to boiling.

Allow to cool and transfer each calibration solution into a 200 ml one-mark volumetric flask.

With calibrated pipettes, add the quantities (volumes) of the mono-elemental standard solutions (4.9 to 4.18) or of commercial available mono-elemental standard solutions of each element shown in Table 2.

Add to each volumetric flask 10 ml of the fusion mixture solution (4.8.2) and 10 ml of hydrochloric acid (4.1).

If an internal reference element is used add, with a calibrated pipette, 10 ml of the internal reference element solution (4.19).

NOTE 1 Refer to NOTE 1 under 7.2.3.

Dilute to the mark with water and mix.

NOTE 2 Refer to NOTE 2 under 7.2.3.

Following this same procedure, also prepare a pure iron solution (labelled F0 in Table 2), to be used to control if the lowest content for each element is enough high to be considered as "different from the zero point".

Strong care should be taken in order to ensure that the quantity of acids remains about the same in the calibration solutions (**namely 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.

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

NOTE 3 The trueness of these calibration functions should be checked 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				
	F0	F1	F2	F3	F4
Fe	*1 000,0 mg* *100,00 %*	*958,3 mg* *95,83 %*	*979,7 mg* *97,97 %*	*971,2 mg* *97,12 %*	*989,7 mg* *98,97 %*
Mn (4.13)	------	20 mg [2,0 %] 20 ml	2 mg [0,2 %] 2 ml	0,02 mg [0,002 %] [a]	0,2 mg [0,02 %] [b]
P (4.16)	------	0,05 mg [0,005 %] [c]	0,1 mg [0,01 %] [d]	0,5 mg [0,05 %] [e]	1 mg [0,1 %] 1 ml
Cu (4.12)	------	0,5 mg [0,05 %] [f]	8 mg [0,8 %] 8 ml	0,05 mg [0,005 %] [g]	1 mg [0,1 %] 1 ml
Ni (4.15)	------	20 mg [2,0 %] 20 ml	5 mg [0,5 %] 5 ml	0,05 mg [0,005 %] [h]	0,5 mg [0,05 %] [i]
Cr (4.10)	------	0,05 mg [0,005 %] [j]	0,5 mg [0,05 %] [k]	16 mg [1,6 %] 16 ml	5 mg [0,5 %] 5 ml
Mo (4.14)	------	0,05 mg [0,005 %] [l]	0,5 mg [0,05 %] [m]	8 mg [0,8 %] 8 ml	1 mg [0,1 %] 1 ml
V (4.18)	------	0,02 mg [0,002 %] [n]	4 mg [0,4 %] 4 ml	0,2 mg [0,02 %] [o]	1 mg [0,1 %] 1 ml
Co (4.11)	------	0,02 mg [0,002 %] [p]	0,1 mg [0,01 %] [q]	1 mg [0,1 %] 1 ml	0,05 mg [0,005 %] [r]
Al (4.9)	------	0,03 mg [0,003 %] [s]	0,1 mg [0,01 %] [t]	3 mg [0,3 %] 3 ml	0,5 mg [0,05 %] [u]
Sn (4.17)	------	1 mg [0,1 %] 1 ml	0,05 mg [0,005 %] [v]	0,01 mg [0,001 %] [w]	0,1 mg [0,01 %] [x]

[a] 2 ml of a 0,01 g/l manganese standard solution
[b] 2 ml of a 0,1 g/l manganese standard solution
[c] 5 ml of a 0,01 g/l phosphorus standard solution
[d] 1 ml of a 0,1 g/l phosphorus standard solution
[e] 5 ml of a 0,1 g/l phosphorus standard solution
[f] 5 ml of a 0,1 g/l copper standard solution
[g] 5 ml of a 0,01 g/l copper standard solution
[h] 5 ml of a 0,01 g/l nickel standard solution
[i] 5 ml of a 0,1 g/l nickel standard solution
[j] 5 ml of a 0,01 g/l chromium standard solution
[k] 5 ml of a 0,1 g/l chromium standard solution
[l] 5 ml of a 0,01 g/l molybdenum standard solution
[m] 5 ml of a 0,1 g/l molybdenum standard solution
[n] 2 ml of a 0,01 g/l vanadium standard solution
[o] 2 ml of a 0,1 g/l vanadium standard solution
[p] 2 ml of a 0,01 g/l cobalt standard solution
[q] 1 ml of a 0,1 g/l cobalt standard solution
[r] 5 ml of a 0,01 g/l cobalt standard solution
[s] 3 ml of a 0,01 g/l aluminium standard solution
[t] 1 ml of a 0,1 g/l aluminium standard solution
[u] 5 ml of a 0,1 g/l aluminium standard solution
[v] 5 ml of a 0,01 g/l tin standard solution
[w] 1 ml of a 0,01 g/l tin standard solution
[x] 1 ml of a 0,1 g/l tin standard solution

8.3 Re-calibration

Drifts in the spectrometer readings shall be corrected by using the re-calibration procedure 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 apparatus

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)
Mn	257,6 or 293,1
P	178,2
Cu	324,7 or 327,4
Ni	231,6
Cr	205,6 or 206,6 or 267,7
Mo	202,0 or 281,6
V	309,3 or 310,2 or 311,1
Co	228,6 or 230,8
Al	394,4 or 396,2
Sn	189,9
Cd	*214,1*
Fe	*271,4*
Sc	*361,4*
Y	*371,0*

NOTE 1 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.

NOTE 2 Other wavelengths may be used, provided that interferences, sensivity, 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 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 a software suitable for regression calculations and calculate the relevant correlation coefficients: these coefficients should be, at least, 0,999.

If this criterion is not conforming, check eventual 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 checked 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 conforming, repeat the test with a re-prepared set of multi-elemental calibration solutions or adapt the analytical range(s).

Table 4 — Trueness control limits

Concentration range %	**Maximum difference (±)** %
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	0,010
0,2 to 0,5	0,018
0,5 to 1,0	0,030
1,0 to 2,0	0,045

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 concerned 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 accepted if all the results for the Certified Reference Material (or Internal Reference Material) concerned are situated in the interval "Certified Value $\pm 2\sigma$", 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 Trueness control

Analyse two other Certified Reference Material (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 measurements of the unknown samples analytical series can start if the results for at least one of the Certified Reference Material concerned are situated in the interval "Certified Value $\pm 2\sigma$".

If abnormal deviations appear for the same element in both of them, reject all the sample solutions and restart a new sample solution 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 abnormal deviations appear, reject the results concerned and restart 9.4.2 and 9.4.3 procedures.

Re-measuring CRM 2 and CRM 3 sample solutions and the drift control sample solution should be carried out before ending each analytical series measurements.

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	Concentration range %	Maximum drift %
all	0,001 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	0,005
	0,2 to 0,5	0,02
	0,5 to 1,0	0,03
	1,0 to 2,0	0,05

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

Sixteen laboratories in eight European countries participated in an inter laboratory validation test programme under the auspices of ECISS/TC 102/WG 10, involving three determinations of eleven elements at several levels (from 8 to 15, depending on the element and its corresponding scope).

NOTE 1 Titanium was also included in the scope of the method sent for the precision test. Nevertheless, for reasons linked with a lack in the trueness of the results produced during this precision test, titanium 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 details of the samples used are 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 (Tables D.1 to D.10).

Except for Phosphorus, 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 Tables 6 to 14.

Table 6 — Manganese — Repeatability limit and reproducibility limits

Manganese content % (mass fraction)	Repeatability limit r	Reproducibility limits R_w	 R
0,005	0,000 2	0,000 5	0,001 5
0,01	0,000 4	0,000 9	0,002 5
0,02	0,000 7	0,001 6	0,004 1
0,05	0,001 7	0,003 2	0,007 8
0,1	0,003 1	0,005 4	0,012 7
0,2	0,005 7	0,009 3	0,020 7
0,5	0,012 9	0,018 9	0,039 5
1,0	0,024	0,032	0,064
2,0	0,044	0,055	0,105

NOTE 2 Phosphorus (Repeatability limit and reproducibility limits): for this element, the correlation coefficients of the logarithmic relationships between the related contents and the repeatability limit (r) and reproducibility limits (R_w and R) of the test results were below the conventional limit (< 0.7). Therefore only the precision data reported in Table D.2 (see Annex D) apply.

Table 7 — Copper — Repeatability limit and reproducibility limits

Copper content % (mass fraction)	Repeatability limit r	Reproducibility limits R_w	 R
0,005	0,000 7	0,000 9	0,001 8
0,01	0,001 1	0,001 5	0,002 8
0,02	0,001 8	0,002 4	0,004 3
0,05	0,003 3	0,004 5	0,007 6
0,1	0,005 3	0,007 3	0,011 7
0,2	0,008 6	0,011 8	0,017 9
0,5	0,016 1	0,022 1	0,031 5
1,0	0,026	0,036	0,048

Table 8 — Nickel — Repeatability limit and reproducibility limits

Nickel content	Repeatability limit	Reproducibility limits	
% (mass fraction)	r	R_w	R
0,01	0,000 8	0,001 2	0,002 1
0,02	0,001 2	0,002 1	0,003 5
0,05	0,002 4	0,004 1	0,006 7
0,1	0,003 8	0,006 9	0,011 2
0,2	0,006 2	0,011 5	0,018 5
0,5	0,011 9	0,022 8	0,036 1
1,0	0,019 4	0,038 1	0,059 9
2,0	0,031 6	0,063 7	0,099 4

Table 9 — Chromium — Repeatability limit and reproducibility limits

Chromium content	Repeatability limit	Reproducibility limits	
% (mass fraction)	r	R_w	R
0,01	0,001 0	0,001 8	0,003 1
0,02	0,001 6	0,002 8	0,005 0
0,05	0,002 9	0,005 0	0,009 4
0,1	0,004 4	0,007 9	0,015 0
0,2	0,006 8	0,012 4	0,024 0
0,5	0,012 2	0,022 6	0,044 8
1,0	0,018 8	0,035 4	0,071 7
2,0	0,029 1	0,055 6	0,114 7

Table 10 — Molybdenum — Repeatability limit and reproducibility limits

Molybdenum content	Repeatability limit	Reproducibility limits	
% (mass fraction)	r	R_w	R
0,005	0,000 7	0,001 2	0,002 2
0,01	0,001 1	0,001 7	0,003 3
0,02	0,001 6	0,002 6	0,005 1
0,05	0,002 8	0,004 4	0,008 9
0,1	0,004 1	0,006 5	0,013 6
0,2	0,006 1	0,009 7	0,020 9
0,5	0,010 3	0,016 4	0,036 6
1,0	0,015 2	0,024 4	0,055 9

Table 11 — Vanadium — Repeatability limit and reproducibility limits

Vanadium content % (mass fraction)	Repeatability limit r	Reproducibility limits	
		R_w	R
0,002	0,000 3	0,000 5	0,001 7
0,005	0,000 6	0,000 9	0,002 5
0,01	0,000 9	0,001 4	0,003 6
0,02	0,001 3	0,002 1	0,004 9
0,05	0,002 3	0,003 6	0,007 5
0,1	0,003 5	0,005 4	0,010 4
0,2	0,005 3	0,008 2	0,014 3
0,5	0,009 2	0,014 0	0,021 9

Table 12 — Cobalt — Repeatability limit and reproducibility limits

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

Table 13 — Aluminium (total) — Repeatability limit and reproducibility limits

Aluminium content % (mass fraction)	Repeatability limit r	Reproducibility limits	
		R_w	R
0,02	0,001 4	0,002 4	0,005 0
0,05	0,002 7	0,005 2	0,009 4
0,1	0,004 5	0,009 5	0,015 1
0,2	0,007 4	0,017 3	0,024 5
0,3	0,009 9	0,024 6	0,032 4

Table 14 — Tin — Repeatability limit and reproducibility limits

Tin content % (mass fraction)	Repeatability limit r	Reproducibility limits R_w	 R
0,001	0,000 3	0,000 5	0,000 7
0,002	0,000 4	0,000 7	0,001 0
0,005	0,000 7	0,001 1	0,001 7
0,01	0,001 1	0,001 6	0,002 6
0,02	0,001 6	0,002 4	0,003 9
0,05	0,002 6	0,003 9	0,006 8
0,1	0,003 9	0,005 7	0,010 2

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:

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

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 equation:

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

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 minutes to one hour, 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 (%)
Mn	0,06 to 0,9	0,12 to 3,0
P	0,36 to 2,8	0,27 to 5,8
Cu	0,11 to 0,9	0,16 to 2,7
Ni	0,06 to 1,0	0,44 to 3,8
Cr	0,05 to 0,9	0,07 to 4,1
Mo	0,16 to 0,8	0,22 to 3,6
V	0,06 to 0,8	0,07 to 3,4
Co	0,25 to 1,0	0,58 to 7,7
Al	0,09 to 1,0	0,20 to 3,6
Sn	0,25 to 3,1	0,30 to 4,6

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 as:

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

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)
Mn	0,002 to 0,5
P	0,015 to 5,0
Cu	0,005 to 1,5
Ni	0,012 to 3,3
Cr	0,006 to 1,1
Mo	0,010 to 1,4
V	0,006 to 0,8
Co	0,012 to 5,8
Al	0,016 to 3,2
Sn	0,011 to 7,3

A.4 Evaluating the limit of detection

A.4.1 Introduction

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)
Mn	0,000 1 to 0,10
P	0,000 3 to 0,33
Cu	0,000 1 to 0,07
Ni	0,000 3 to 0,06
Cr	0,000 1 to 0,08
Mo	0,000 2 to 0,11
V	0,000 1 to 0,04
Co	0,000 2 to 0,23
Al	0,000 3 to 0,09
Sn	0,000 2 to 0,23

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. 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

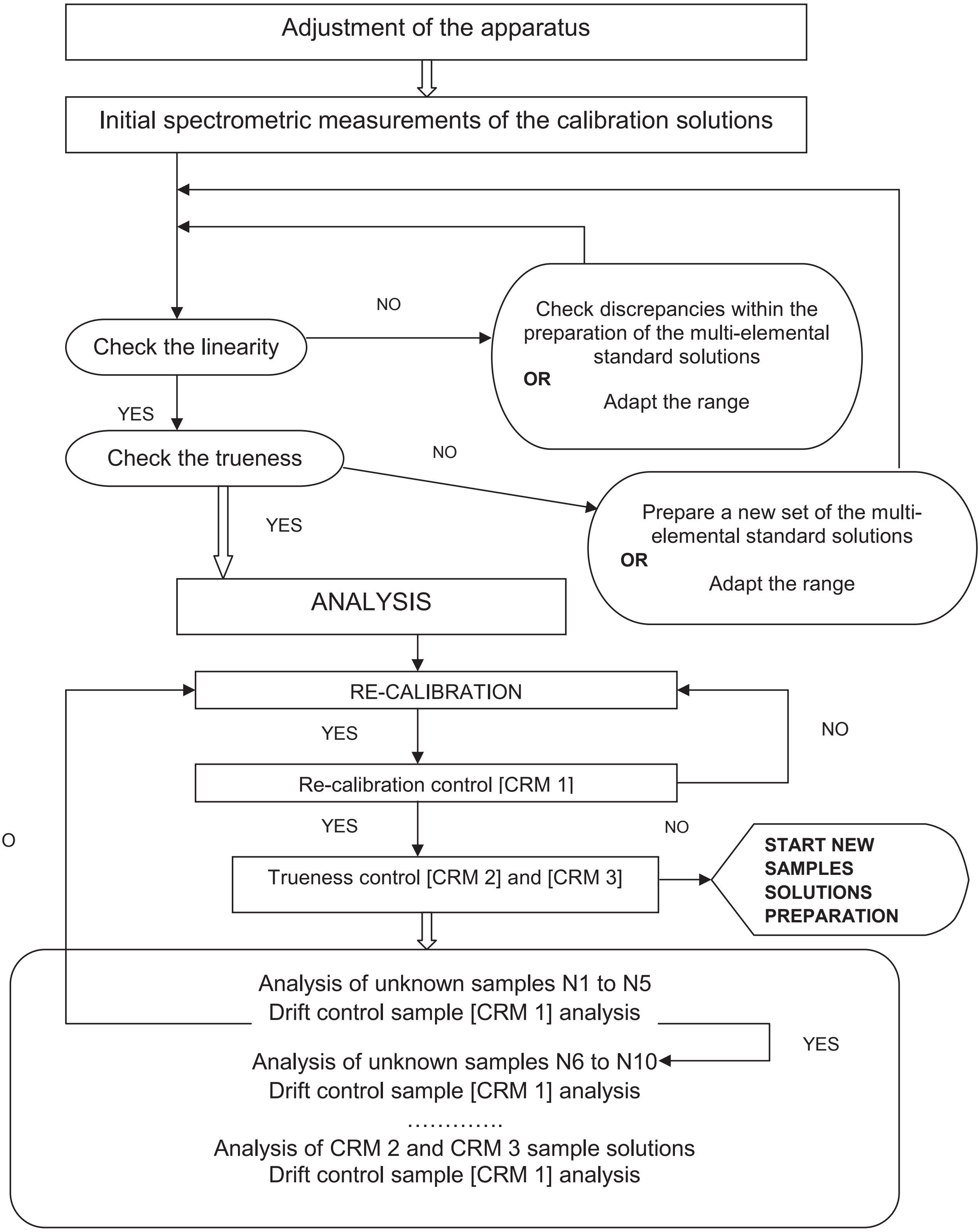
Operate as follows:

- 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, the limit of detection (C_{lim}) is calculated according to the equation:

$$C_{lim} = \frac{4.65 \times \sigma_0 \times C_x}{I_x - I_0}$$

Annex B
(normative)

Synoptic of the operations related to Clause 9



Annex C
(informative)

Test samples used for the validation precision test

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

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

Sample label	C	Si	Mn	S	P	Cu	Ni	Cr	Mo	Ti	V	Co	Al	Sn	Others
A [ECRM 035-2]	1,28	0,22	0,31	0,011	0,004	0,009	0,020	0,010	0,006	0,003			0,019		As: 0,002
B [JK 3B]	0,74	0,25	0,80	0,007	0,010	0,018	0,059	0,053	0,005			0,005	0,004	0,004	
C [IRM R8]	0,44	0,33	1,32	0,047	0,098	0,47	0,55	0,70	0,45	0,23	0,11		0,30	0,097	As: 0,09; Nb: 0,06
D [ECRM 097-1]			0,006	0,002	0,002	0,002	0,003	0,002				0,004			As: 0,005; B: 0,000 3
E [ECRM 090-1]	1,05	0,28	0,23	0,009	0,013		0,053	0,12	0,009		0,20				
F [ECRM 191-1]	0,013	3,14	0,025	0,002	0,011	0,008	0,018	0,025		0,009			0,40		As: 0,003
G [ECRM 193-1]	0,14	0,40	0,97	0,009	0,006	0,60	1,18	0,18	0,35			0,007	0,026		As: 0,006; Nb: 0,02
H [ECRM 195-1]	0,76	0,47	0,57	0,012	0,016	0,035	0,33	1,57	0,77		0,31				Ca: 0,002; Pb: 0,001; Zn: 0,005
I [BCS 111]	0,026	0,025	0,16	0,005	0,003	0,017	0,039	0,020	0,000 8	0,000 4	0,000 9	0,014	0,035	0,001 5	As: 0,002
J [BCS 453/1]	0,16	0,34	1,38	0,026	0,044	0,10	0,11	0,26	0,081	0,073				0,022	As: 0,05; W: 0,3
K [BCS 452/1]	0,32	0,06	1,30	0,017	0,035	0,22	0,19	0,067	0,054	0,031				0,094	As: 0,015; W 0,05
L [BCS 459/1]	0,47	0,64	0,91	0,048	0,048						0,059	0,089			B: 0,01; Nb: 0,01; Pb: 0,004; Zr: 0,07; Sb: 0,01
M [IRM 41]	0,33	0,25	0,59	0,003	0,009		1,57	0,83	0,032	< 0,002	< 0,01	0,045	< 0,005	0,009 5	
N [IRM 66]	0,29	0,23	0,61	0,003	0,009		0,17	1,06	0,24	0,003	0,007	0,025	0,008	0,003	
O [IRM HOG]			0,15		0,005	0,02	1,9	0,02	0,57						

Annex D
(informative)

Detailed results obtained from the validation precision test

Table D.1 — Manganese

	A	B	C	D	E	F	G
Mean, %	0,303 7	0,796 5	1,282 3	0,006 15	0,225 7	0,027 40	0,975 5
$\sigma(r)$, %	0,003 2	0,007 2	0,011 3	0,000 13	0,002 7	0,000 24	0,007 8
$\sigma(R_w)$, %	0,003 9	0,010 3	0,014 3	0,000 29	0,003 0	0,000 54	0,008 3
$\sigma(R)$, %	0,007 6	0,028 8	0,029 3	0,000 81	0,007 3	0,001 34	0,019 1
r, %	0,009 0	0,020 1	0,031 6	0,000 36	0,007 5	0,000 66	0,021 8
R_w, %	0,010 8	0,028 7	0,040 2	0,000 81	0,008 3	0,001 51	0,023 3
R, %	0,021 2	0,080 6	0,082 1	0,002 26	0,020 4	0,003 76	0,053 4
CV (R)	2,50	**3,62**	2,29	13,15	3,23	4,90	1,95
Aim CV (R)	2,23	1,60	1,36	8,63	2,47	5,14	1,49
Max CV (R)	4,91	3,51	2,98	18,96	5,44	11,30	3,27

Table D.1 — Manganese *(continued)*

	H	I	J	K	L	M	N	O
Mean, %	0,575 8	0,155 5	1,383 8	1,296 1	0,912 7	0,568 3	0,620 4	0,206 6
$\sigma(r)$, %	0,004 6	0,001 5	0,009 6	0,015 7	0,007 8	0,006 0	0,005 2	0,001 6
$\sigma(R_w)$, %	0,007 3	0,002 4	0,018 1	0,015 4	0,009 9	0,009 0	0,009 1	0,004 5
$\sigma(R)$, %	0,015 1	0,005 3	0,026 9	0,024 5	0,019 0	0,020 1	0,020 8	0,008 7
r, %	0,012 8	0,004 1	0,026 9	0,043 9	0,021 9	0,016 9	0,014 5	0,004 5
R_w, %	0,020 4	0,006 6	0,050 6	0,043 1	0,027 7	0,025 1	0,025 4	0,012 7
R, %	0,042 3	0,014 9	0,075 3	0,068 7	0,053 1	0,056 4	0,058 2	0,024 5
CV (R)	2,63	3,43	1,94	1,89	2,08	3,54	3,35	4,23
Aim CV (R)	1,79	2,82	1,32	1,35	1,52	1,80	1,74	2,55
Max CV (R)	3,93	6,19	2,90	2,97	3,35	3,95	3,83	5,61

Table D.2 — Phosphorus

	A	**B**	**C**	**E**	**F**	**G**	**H**
Mean, %	0,004 27	0,009 56	0,090 7	0,012 10	0,009 82	0,005 89	0,015 51
$\sigma(r)$, %	0,000 26	0,000 43	0,002 2	0,000 64	0,001 04	0,000 93	0,000 71
$\sigma(R_w)$, %	0,000 75	0,000 79	0,003 1	0,000 89	0,001 18	0,000 65	0,001 36
$\sigma(R)$, %	0,000 78	0,001 07	0,007 7	0,001 37	0,002 13	0,000 91	0,001 16
r, %	0,000 72	0,001 21	0,006 0	0,001 80	0,002 92	0,002 61	0,001 99
R_w, %	0,002 10	0,002 22	0,008 6	0,002 48	0,003 31	0,001 82	0,003 81
R, %	0,002 18	0,003 00	0,021 6	0,003 85	0,005 96	0,002 55	0,003 24
CV (R)	18,26	11,21	**8,50**	11,35	**21,68**	15,46	7,46
Aim CV (R)	9,79	7,40	3,39	6,82	7,34	8,75	6,26
Max CV (R)	21,52	16,27	7,46	14,99	16,12	19,24	13,76

Table D.2 — Phosphorus *(continued)*

	I	**J**	**K**	**L**	**M**	**N**	**O**
Mean, %	0,003 46	0,041 6	0,033 4	0,047 9	0,009 47	0,008 84	0,003 88
$\sigma(r)$, %	0,000 54	0,001 4	0,001 0	0,001 0	0,000 45	0,000 62	0,000 33
$\sigma(R_w)$, %	0,000 61	0,001 3	0,000 8	0,001 2	0,000 41	0,000 78	0,000 52
$\sigma(R)$, %	0,000 89	0,002 1	0,001 1	0,002 4	0,000 72	0,001 31	0,000 71
r, %	0,001 51	0,003 9	0,002 9	0,002 9	0,001 25	0,001 72	0,000 92
R_w, %	0,001 70	0,003 4	0,002 3	0,003 4	0,001 13	0,002 18	0,001 46
R, %	0,002 75	0,006 0	0,003 0	0,006 6	0,002 03	0,003 67	0,001 98
CV (R)	**28,38**	5,15	3,23	4,92	7,65	14,81	18,17
Aim CV (R)	10,53	4,45	4,80	4,24	7,43	7,61	10,12
Max CV (R)	23,15	9,77	10,55	9,31	16,33	16,72	22,23

Table D.3 — Copper

	A	B	C	E	F	G	H
Mean, %	0,008 90	0,016 98	0,455 1	0,043 2	0,008 84	0,597 8	0,037 5
$\sigma(r)$, %	0,000 57	0,000 53	0,007 9	0,000 8	0,000 59	0,008 5	0,001 3
$\sigma(R_w)$, %	0,000 53	0,000 68	0,009 6	0,001 8	0,000 63	0,009 1	0,001 6
$\sigma(R)$, %	0,001 68	0,001 22	0,014 0	0,002 2	0,001 00	0,015 6	0,002 3
r, %	0,001 60	0,001 49	0,022 0	0,002 3	0,001 65	0,023 9	0,003 7
R_w, %	0,001 48	0,001 92	0,027 0	0,005 0	0,001 75	0,025 4	0,004 4
R, %	0,004 70	0,003 43	0,039 3	0,006 2	0,002 81	0,043 8	0,006 4
CV (R)	**18,85**	7,21	3,09	5,12	11,34	2,62	6,08
Aim CV (R)	7,59	6,07	1,94	4,39	7,61	1,77	4,61
Max CV (R)	16,68	13,33	4,27	9,65	16,72	3,88	10,13

Table D.3 — Copper *(continued)*

	I	J	K	L	M	N	O
Mean, %	0,017 40	0,098 8	0,216 8	0,009 55	0,094 3	0,058 2	0,024 76
$\sigma(r)$, %	0,000 47	0,002 2	0,002 8	0,000 37	0,001 3	0,000 8	0,000 44
$\sigma(R_w)$, %	0,000 79	0,002 2	0,006 7	0,000 65	0,001 5	0,001 0	0,000 83
$\sigma(R)$, %	0,00098	0,003 3	0,007 2	0,001 21	0,003 2	0,002 2	0,001 72
r, %	0,001 30	0,006 0	0,007 8	0,001 03	0,003 6	0,002 1	0,001 23
R_w, %	0,002 21	0,006 2	0,018 9	0,001 82	0,004 1	0,002 9	0,002 31
R, %	0,002 73	0,009 2	0,020 2	0,003 38	0,008 9	0,006 1	0,004 83
CV (R)	5,61	3,31	3,33	12,65	3,37	3,76	6,97
Aim CV (R)	6,02	3,30	2,51	7,41	3,35	3,96	5,32
Max CV (R)	13,22	7,24	5,51	16,28	7,36	8,70	11,70

Table D.4 — Nickel

	A	**B**	**C**	**E**	**F**	**G**	**H**
Mean, %	0,019 37	0,057 8	0,533 2	0,051 4	0,017 68	1,176 4	0,330 5
$\sigma(r)$, %	0,000 87	0,000 7	0,005 6	0,000 9	0,000 30	0,011 9	0,004 8
$\sigma(R_w)$, %	0,000 93	0,001 1	0,007 5	0,001 0	0,000 93	0,019 5	0,006 8
$\sigma(R)$, %	0,001 26	0,002 4	0,015 3	0,002 1	0,001 46	0,024 1	0,010 2
r, %	0,002 59	0,002 1	0,015 7	0,002 5	0,000 83	0,033 3	0,013 5
R_w, %	0,003 09	0,003 0	0,021 1	0,002 7	0,002 62	0,054 5	0,019 1
R, %	0,003 54	0,006 9	0,043 0	0,006 0	0,004 09	0,067 5	0,028 6
CV (R)	6,52	4,23	2,88	4,18	8,27	2,05	3,10
Aim CV (R)	5,80	3,97	1,84	4,13	5,98	1,40	2,17
Max CV (R)	12,74	8,72	4,04	9,08	13,15	3,07	4,77

Table D.4 — Nickel *(continued)*

	I	**J**	**K**	**L**	**M**	**N**	**O**
Mean, %	0,038 8	0,107 0	0,191 0	0,019 29	1,542 3	0,179 5	1,914 4
$\sigma(r)$, %	0,000 5	0,001 0	0,002 6	0,000 56	0,007 3	0,001 1	0,009 7
$\sigma(R_w)$, %	0,001 2	0,002 3	0,003 3	0,001 05	0,016 4	0,003 1	0,031 7
$\sigma(R)$, %	0,001 9	0,003 6	0,005 5	0,001 31	0,027 1	0,005 1	0,042 7
r, %	0,001 4	0,002 7	0,007 3	0,001 58	0,020 5	0,003 0	0,027 1
R_w, %	0,003 3	0,006 3	0,009 2	0,002 93	0,046 0	0,008 7	0,088 8
R, %	0,005 4	0,010 1	0,015 4	0,003 67	0,076 0	0,014 3	0,119 6
CV (R)	5,01	3,37	2,88	6,80	1,76	2,85	2,23
Aim CV (R)	4,56	3,20	2,62	5,80	1,27	2,68	1,18
Max CV (R)	10,01	7,04	5,76	12,76	2,79	5,89	2,59

Table D.5 — Chromium

	A	B	C	E	F	G	H
Mean, %	0,011 07	0,052 2	0,704 4	0,121 7	0,026 5	0,183 8	1,568 7
$\sigma(r)$, %	0,000 87	0,001 1	0,006 9	0,001 2	0,000 4	0,002 3	0,010 6
$\sigma(R_w)$, %	0,000 66	0,001 3	0,010 4	0,003 4	0,001 6	0,003 1	0,019 4
$\sigma(R)$, %	0,001 02	0,002 9	0,016 2	0,005 7	0,002 0	0,007 3	0,041 7
r, %	0,002 45	0,003 1	0,019 4	0,003 3	0,001 2	0,006 5	0,029 7
R_w, %	0,001 86	0,003 6	0,029 2	0,009 4	0,004 6	0,008 8	0,054 4
R, %	0,002 86	0,008 0	0,045 4	0,016 1	0,005 7	0,020 4	0,116 7
CV (R)	9,22	5,48	2,30	4,72	7,66	3,96	2,66
Aim CV (R)	7,04	4,11	1,67	3,07	5,20	2,66	1,26
Max CV (R)	15,47	9,03	3,67	6,74	11,43	5,84	2,78

Table D.5 — Chromium *(continued)*

	I	J	K	L	M	N	O
Mean, %	0,020 13	0,260 5	0,068 0	0,022 33	0,828 3	1,052 9	0,020 50
$\sigma(r)$, %	0,000 53	0,001 5	0,001 0	0,000 31	0,006 6	0,009 7	0,001 37
$\sigma(R_w)$, %	0,000 82	0,003 8	0,001 4	0,001 02	0,013 9	0,015 7	0,002 24
$\sigma(R)$, %	0,001 38	0,009 9	0,002 3	0,002 13	0,027 1	0,030 4	0,005 55
r, %	0,001 49	0,004 1	0,002 7	0,000 87	0,018 6	0,027 3	0,003 85
R_w, %	0,002 29	0,010 6	0,003 9	0,002 85	0,038 9	0,043 9	0,006 28
R, %	0,003 87	0,027 8	0,006 3	0,005 96	0,075 8	0,085 0	0,015 55
CV (R)	6,86	3,81	3,33	9,54	3,27	2,88	**27,09**
Aim CV (R)	5,72	2,35	3,75	5,52	1,58	1,45	5,68
Max CV (R)	12,57	5,18	8,24	12,13	3,47	3,19	12,49

Table D.6 — Molybdenum

	A	B	C	E	G	H
Mean, %	0,005 62	0,004 84	0,455 5	0,007 68	0,348 9	0,769 5
$\sigma(r)$, %	0,000 48	0,000 23	0,003 9	0,000 31	0,004 1	0,005 8
$\sigma(R_w)$, %	0,000 60	0,000 45	0,006 4	0,000 58	0,005 4	0,009 5
$\sigma(R)$, %	0,000 91	0,000 87	0,013 9	0,001 01	0,008 2	0,018 4
r, %	0,001 36	0,000 64	0,010 9	0,000 86	0,014 4	0,016 3
R_w, %	0,001 69	0,001 26	0,018 0	0,001 62	0,015 1	0,026 7
R, %	0,002 56	0,002 44	0,039 0	0,002 82	0,023 0	0,051 5
CV (R)	16,28	18,00	3,06	13,11	2,36	2,39
Aim CV (R)	8,90	9,37	1,94	7,99	2,13	1,62
Max CV (R)	19,56	20,60	4,26	17,55	4,68	3,56

Table D.6 — Molybdenum *(continued)*

	J	K	M	N	O
Mean, %	0,076 5	0,052 9	0,026 6	0,249 1	0,563 9
$\sigma(r)$, %	0,001 0	0,001 2	0,000 4	0,002 2	0,002 8
$\sigma(R_w)$, %	0,001 7	0,001 1	0,000 8	0,004 8	0,004 7
$\sigma(R)$, %	0,003 7	0,002 6	0,002 1	0,008 3	0,017 9
r, %	0,002 9	0,003 2	0,001 2	0,006 1	0,008 0
R_w, %	0,004 7	0,003 2	0,002 1	0,013 4	0,013 3
R, %	0,010 3	0,007 2	0,005 9	0,023 3	0,050 2
CV (R)	4,80	4,85	7,95	3,34	3,18
Aim CV (R)	3,60	4,09	5,19	2,39	1,80
Max CV (R)	7,91	8,99	11,41	5,26	3,96

Table D.7 — Vanadium

	B	C	E	J	H	L	N	O
Mean, %	0,002 14	0,103 6	0,201 8	0,002 99	0,309 3	0,057 1	0,004 10	0,002 02
$\sigma(r)$, %	0,000 19	0,001 2	0,002 2	0,000 12	0,002 7	0,000 7	0,000 17	0,000 11
$\sigma(R_w)$, %	0,000 61	0,003 5	0,002 6	0,000 36	0,004 7	0,001 2	0,000 52	0,000 18
$\sigma(R)$, %	0,000 79	0,003 7	0,004 7	0,000 72	0,009 5	0,001 8	0,000 72	0,000 65
r, %	0,000 53	0,003 2	0,006 3	0,000 35	0,007 6	0,002 0	0,000 49	0,000 32
R_w, %	0,001 70	0,009 8	0,007 4	0,001 01	0,013 1	0,003 5	0,001 46	0,000 50
R, %	0,002 21	0,010 2	0,013 1	0,002 02	0,026 6	0,005 1	0,002 02	0,001 82
CV (R)	**36,87**	3,53	2,32	24,19	3,07	3,20	17,56	**32,21**
Aim CV (R)	12,43	3,24	2,57	11,08	2,22	3,98	9,93	12,68
Max CV (R)	27,32	7,12	5,65	24,35	4,88	8,76	21,82	27,87

Table D.8 — Cobalt

	A	B	C	D	E	F	G
Mean, %	0,002 69	0,004 35	0,007 58	0,003 35	0,006 12	0,002 80	0,006 43
$\sigma(r)$, %	0,000 08	0,000 14	0,000 45	0,000 09	0,000 19	0,000 10	0,000 21
$\sigma(R_w)$, %	0,000 09	0,000 18	0,000 58	0,000 31	0,000 32	0,000 12	0,000 34
$\sigma(R)$, %	0,000 25	0,000 95	0,000 69	0,000 40	0,000 60	0,000 29	0,000 79
r, %	0,000 23	0,000 39	0,001 31	0,000 26	0,000 54	0,000 29	0,000 59
R_w, %	0,000 24	0,000 50	0,001 63	0,000 86	0,000 91	0,000 33	0,000 96
R, %	0,000 70	0,002 65	0,001 93	0,001 11	0,001 68	0,000 82	0,002 21
CV (R)	9,32	**22,24**	9,12	11,91	9,79	10,41	12,27
Aim CV (R)	11,49	9,80	8,02	10,65	8,64	11,33	8,49
Max CV (R)	25,26	21,55	17,63	23,41	18,99	24,90	18,67

Table D.8 — Cobalt *(continued)*

	H	I	J	K	L	M	N	O
Mean, %	0,005 55	0,013 44	0,004 78	0,003 67	0,088 1	0,042 0	0,022 01	0,005 96
$\sigma(r)$, %	0,000 24	0,000 28	0,000 32	0,000 17	0,001 2	0,000 6	0,000 73	0,000 43
$\sigma(R_w)$, %	0,000 29	0,000 62	0,000 28	0,000 38	0,002 5	0,000 7	0,000 92	0,000 33
$\sigma(R)$, %	0,000 89	0,001 01	0,000 78	0,000 83	0,002 8	0,001 8	0,002 17	0,000 62
r, %	0,000 66	0,000 78	0,000 90	0,000 47	0,003 4	0,001 6	0,002 05	0,001 21
R_w, %	0,000 82	0,001 75	0,000 79	0,001 07	0,007 1	0,002 1	0,002 58	0,000 93
R, %	0,002 48	0,002 84	0,002 20	0,002 34	0,007 8	0,004 9	0,006 07	0,001 74
CV (R)	15,97	7,55	16,40	**22,73**	3,17	4,20	9,85	10,46
Aim CV (R)	8,94	6,58	9,41	10,32	3,43	4,43	5,54	8,72
Max CV (R)	19,64	14,46	20,68	22,67	7,53	9,74	12,19	19,16

Table D.9 — Aluminium (total)

	A	B	C	G	I	N
Mean, %	0,018 51	0,003 93	0,290 4	0,028 7	0,033 5	0,009 04
$\sigma(r)$, %	0,000 30	0,000 42	0,003 1	0,000 9	0,001 0	0,000 33
$\sigma(R_w)$, %	0,000 71	0,000 55	0,008 4	0,001 4	0,001 2	0,000 97
$\sigma(R)$, %	0,001 04	0,001 38	0,010 5	0,005 0	0,002 0	0,002 97
r, %	0,000 84	0,001 17	0,008 7	0,002 4	0,002 7	0,000 93
R_w, %	0,001 97	0,001 53	0,023 6	0,004 0	0,003 3	0,002 70
R, %	0,002 90	0,003 86	0,029 4	0,014 1	0,005 6	0,008 33
CV (R)	5,60	**35,12**	3,62	**17,59**	5,93	**32,89**
Aim CV (R)	5,89	10,08	2,27	5,06	4,79	7,55
Max CV (R)	12,94	22,15	4,98	11,12	10,53	16,59

Table D.10 — Tin

	B	C	E	G	H	I
Mean, %	0,004 24	0,099 1	0,004 72	0,003 52	0,002 21	0,001 72
$\sigma(r)$, %	0,000 25	0,001 4	0,000 21	0,000 20	0,000 27	0,000 14
$\sigma(R_w)$, %	0,000 34	0,002 2	0,000 39	0,000 27	0,000 20	0,000 34
$\sigma(R)$, %	0,000 45	0,003 8	0,000 44	0,000 50	0,000 40	0,000 60
r, %	0,000 69	0,004 0	0,000 60	0,000 56	0,000 75	0,000 38
R_w, %	0,000 95	0,006 2	0,001 08	0,000 74	0,000 57	0,000 97
R, %	0,001 26	0,010 8	0,001 22	0,001 40	0,001 11	0,001 68
CV (R)	10,61	3,88	9,24	14,16	18,04	**34,79**
Aim CV (R)	9,62	3,29	9,45	10,47	12,31	13,41
Max CV (R)	21,57	7,24	20,77	23,01	27,05	29,47

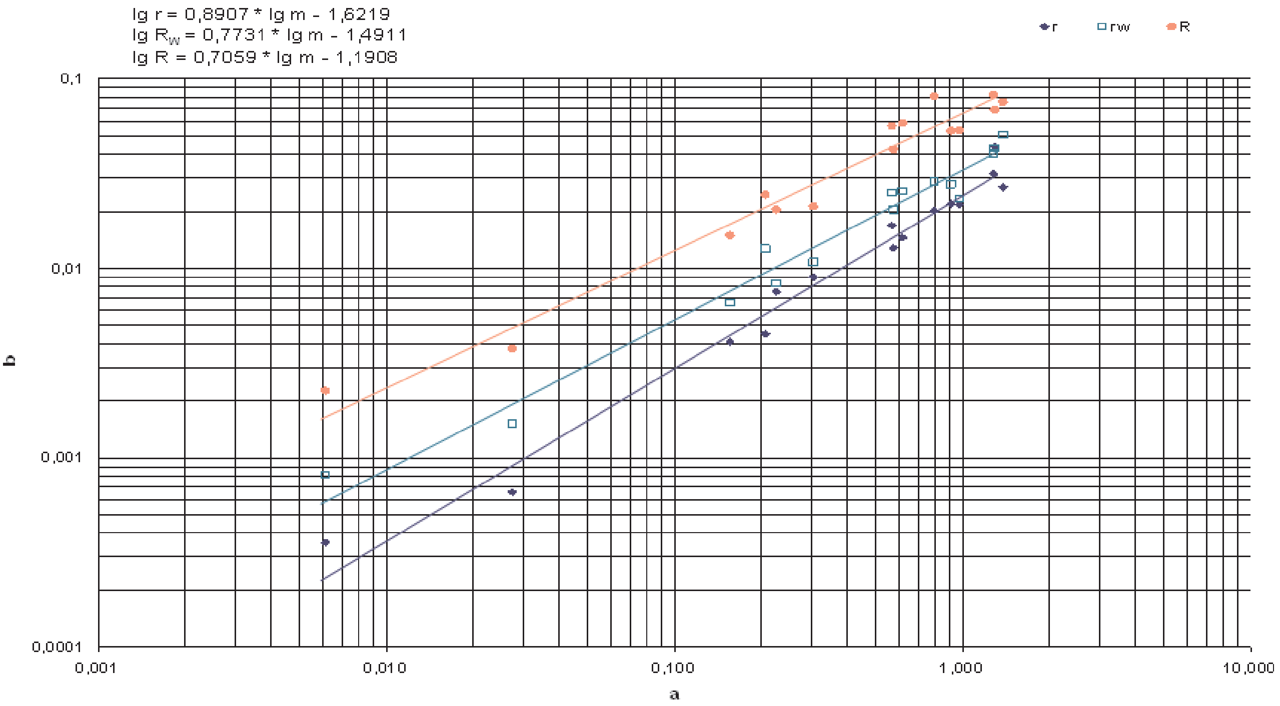
Table D.10 — Tin *(continued)*

	J	K	L	M	N	O
Mean, %	0,021 21	0,093 5	0,001 99	0,008 81	0,006 36	0,002 53
$\sigma(r)$, %	0,000 51	0,001 7	0,000 13	0,000 42	0,000 11	0,000 31
$\sigma(R_w)$, %	0,000 77	0,001 8	0,000 20	0,000 91	0,000 34	0,000 30
$\sigma(R)$, %	0,001 63	0,003 5	0,000 28	0,000 97	0,000 64	0,000 42
r, %	0,001 42	0,004 9	0,000 35	0,001 18	0,000 32	0,000 88
R_w, %	0,002 16	0,005 0	0,000 56	0,002 55	0,000 94	0,000 84
R, %	0,004 55	0,009 8	0,000 79	0,002 71	0,001 79	0,001 19
CV (R)	7,67	3,74	14,09	11,01	10,02	16,72
Aim CV (R)	5,62	3,36	12,74	7,62	8,52	11,73
Max CV (R)	12,35	7,38	28,01	16,74	18,74	25,78

Annex E
(informative)

Graphical representation of the precision data

Figures E.1 to E.9 indicate the logarithmic relationships between the contents of each element (m) and the corresponding repeatability (*r*) and reproducibility parameters (R_w and *R*).

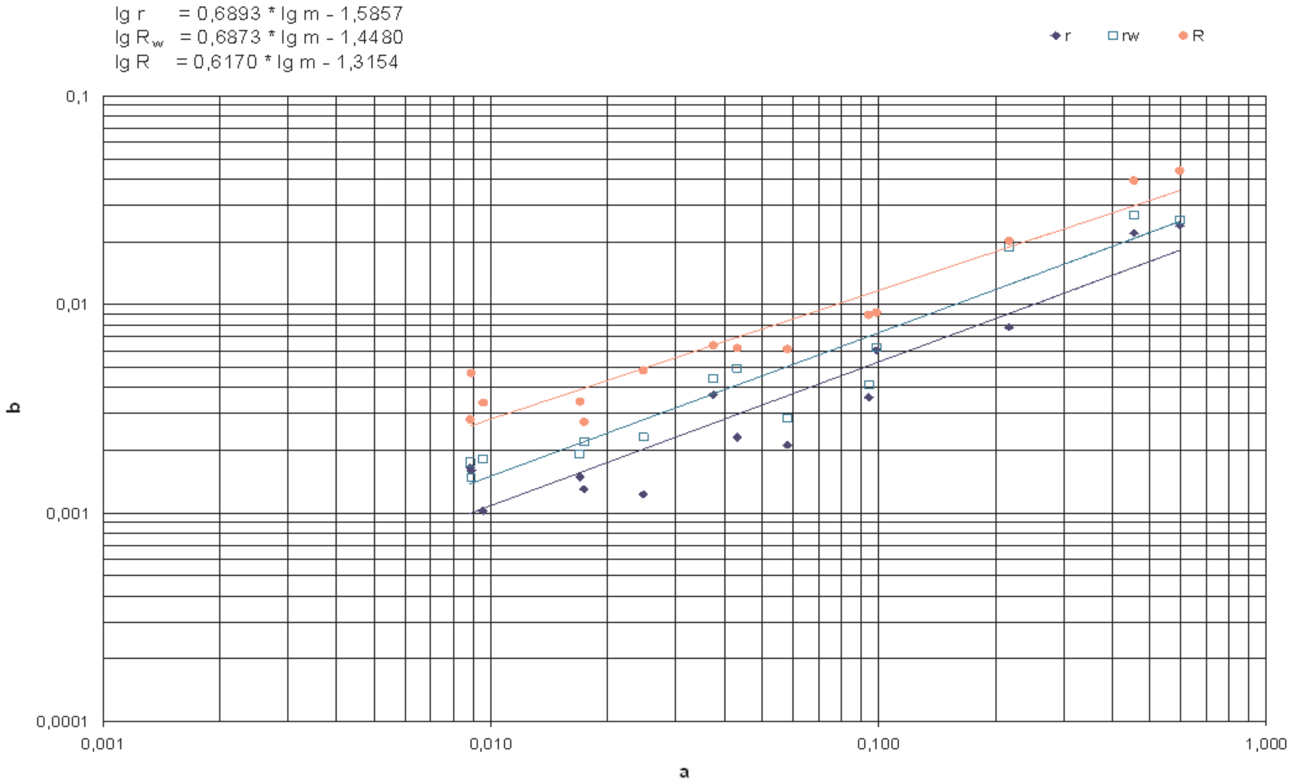


Key

a Mn content % (m/m)

b Precision (%)

Figure E.1 — Manganese

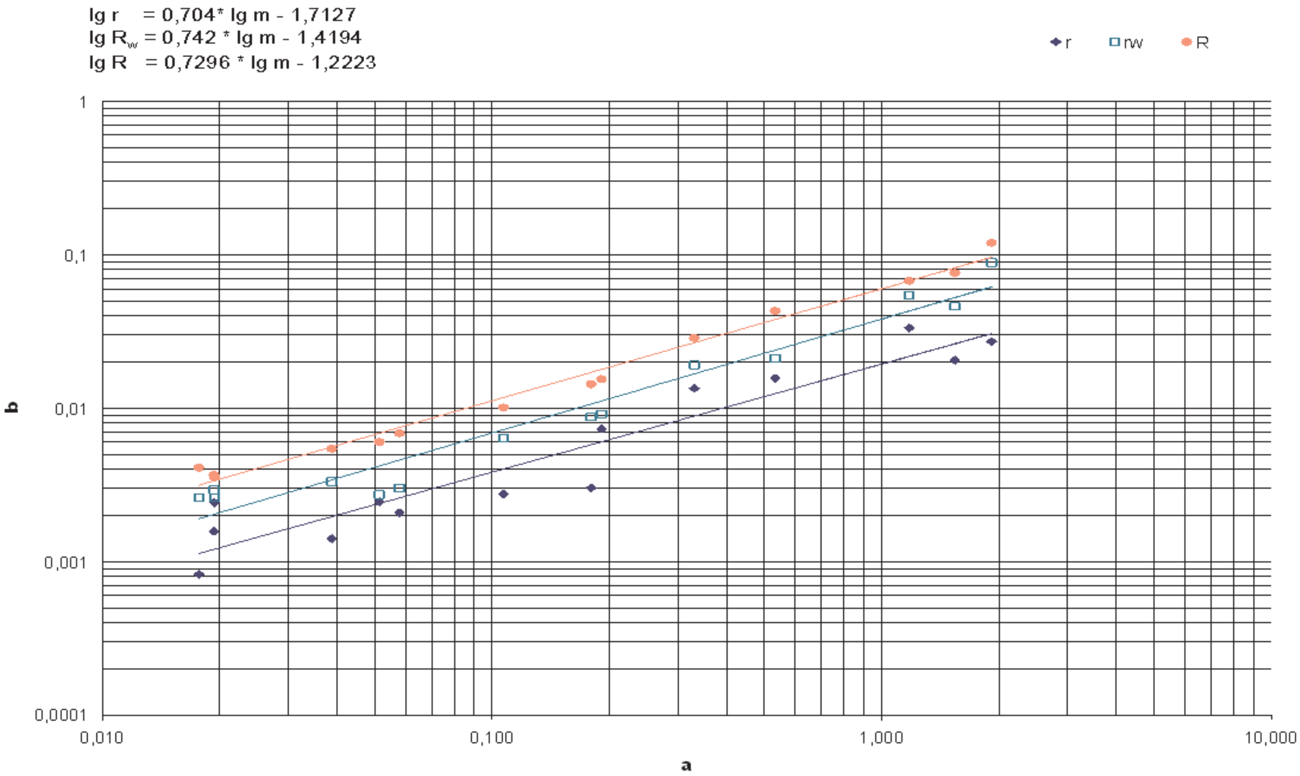


Key

a Cu content % (m/m)

b Precision (%)

Figure E.2 — Copper

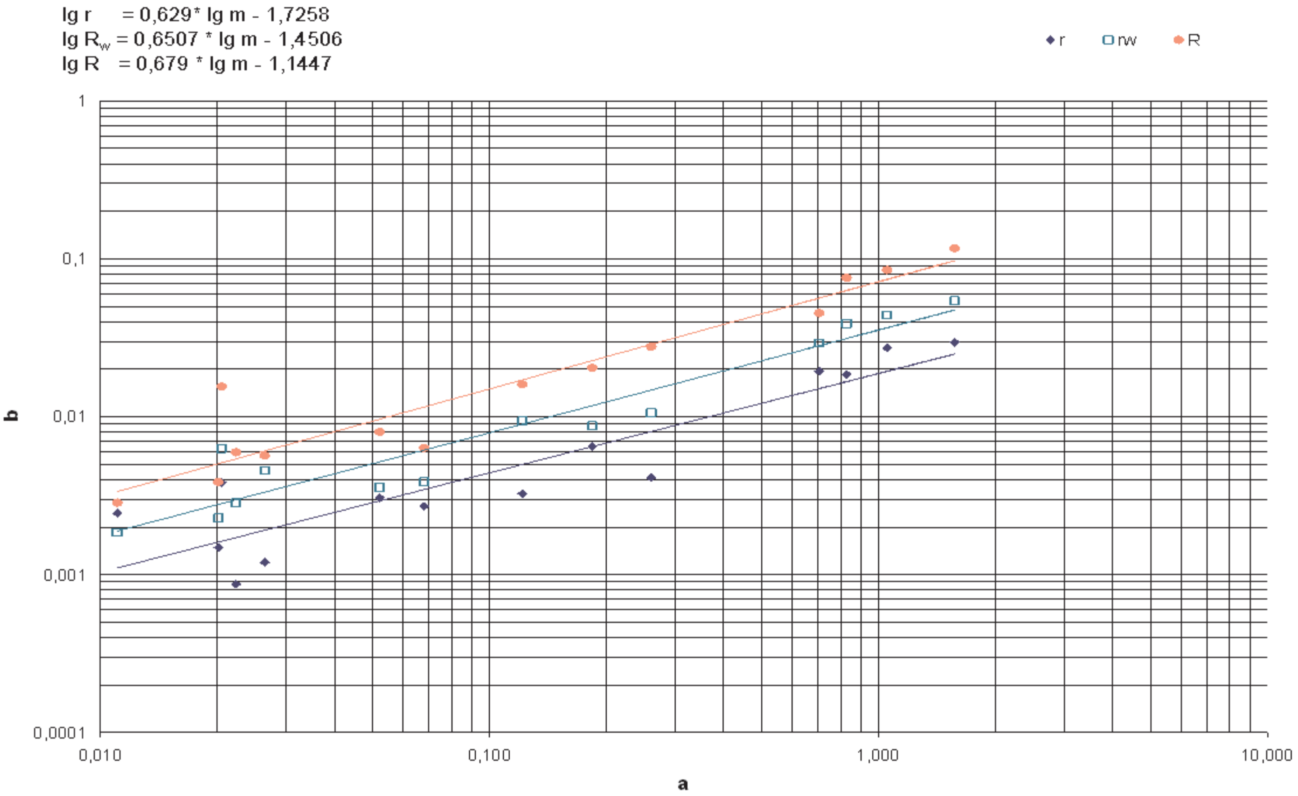


Key

a Ni content % (m/m)

b Precision (%)

Figure E.3 — Nickel

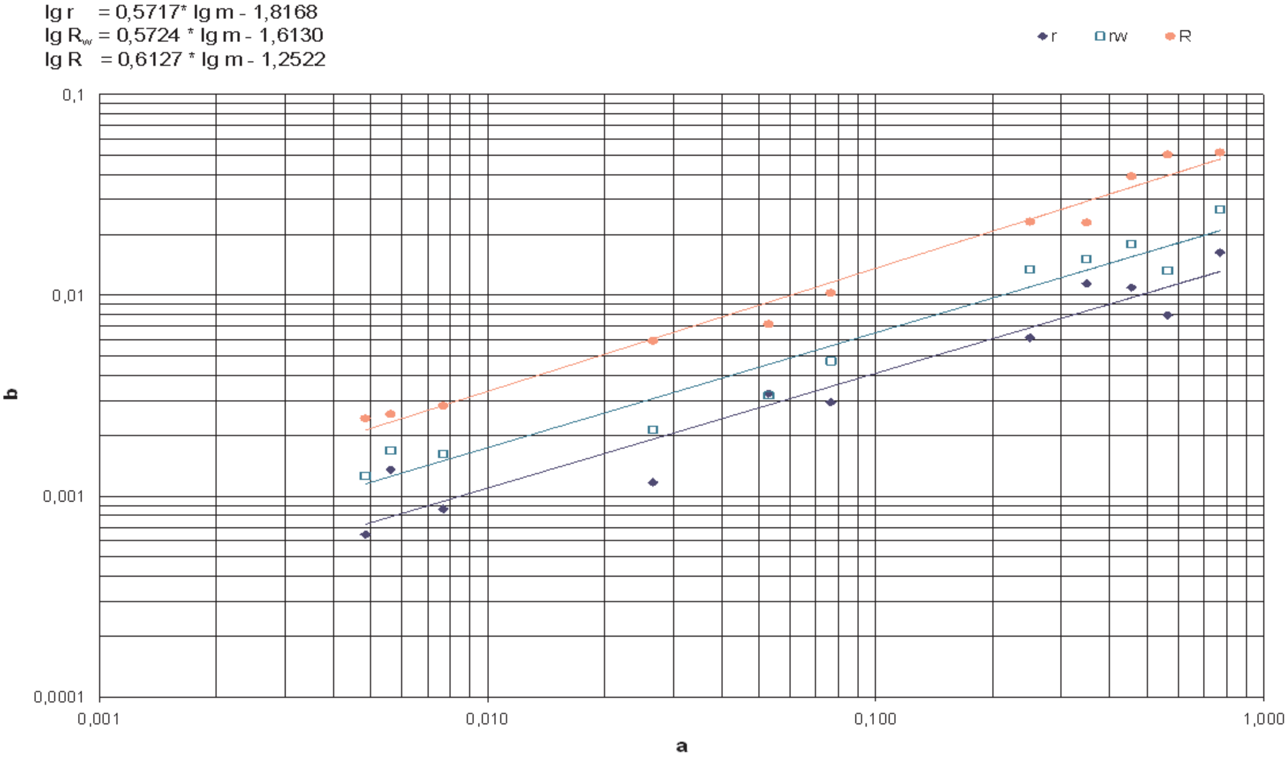


Key

a Cr content % (m/m)

b Precision (%)

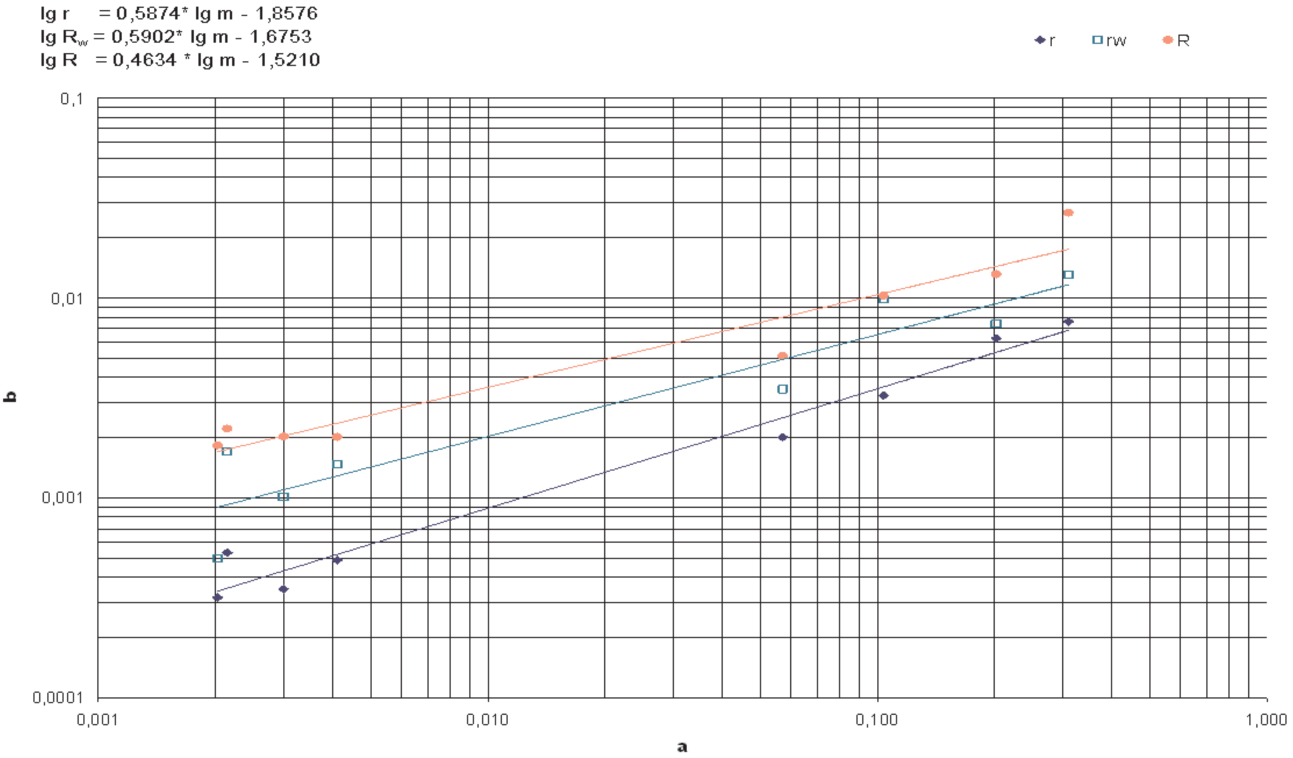
Figure E.4 — Chromium



Key

a	Mo content % (m/m)
b	Precision (%)

Figure E.5 — Molybdenum

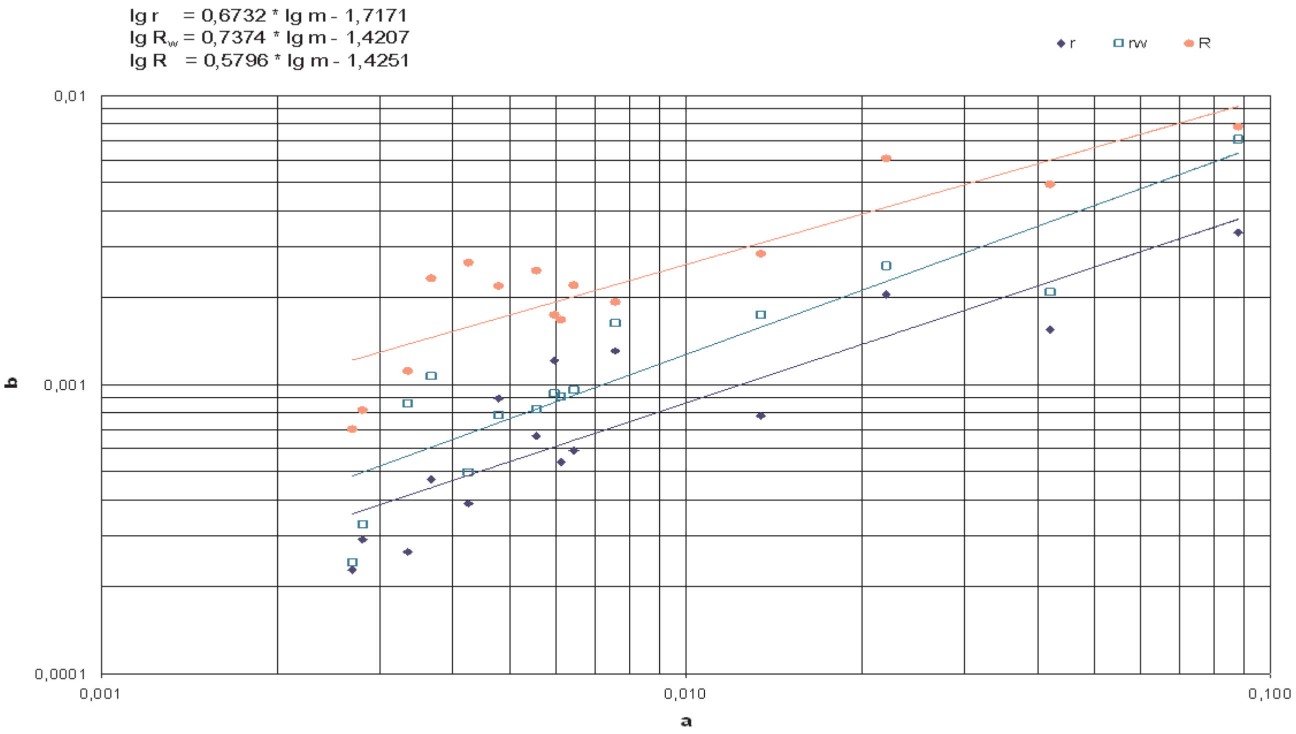


Key

a V content % (m/m)

b Precision (%)

Figure E.6 — Vanadium

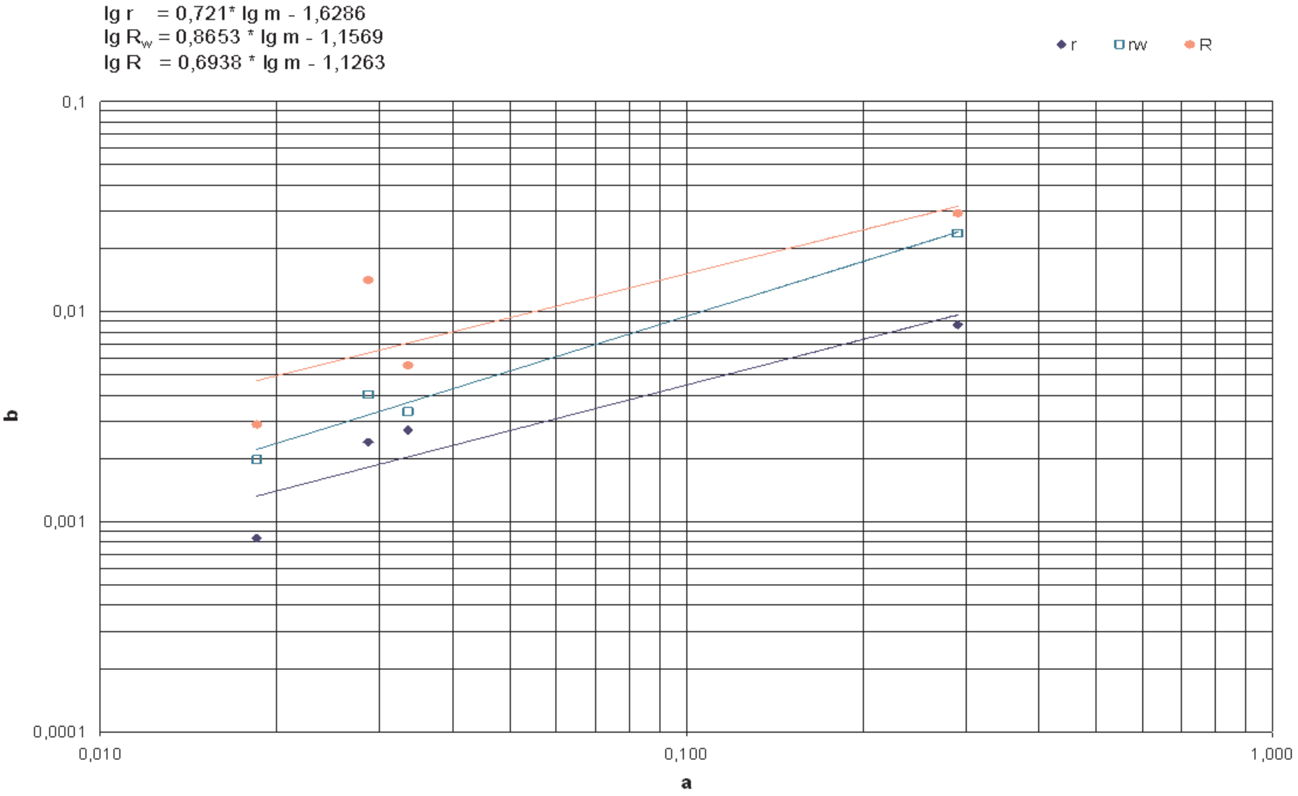


Key

a Co content % (m/m)

b Precision (%)

Figure E.7 — Cobalt

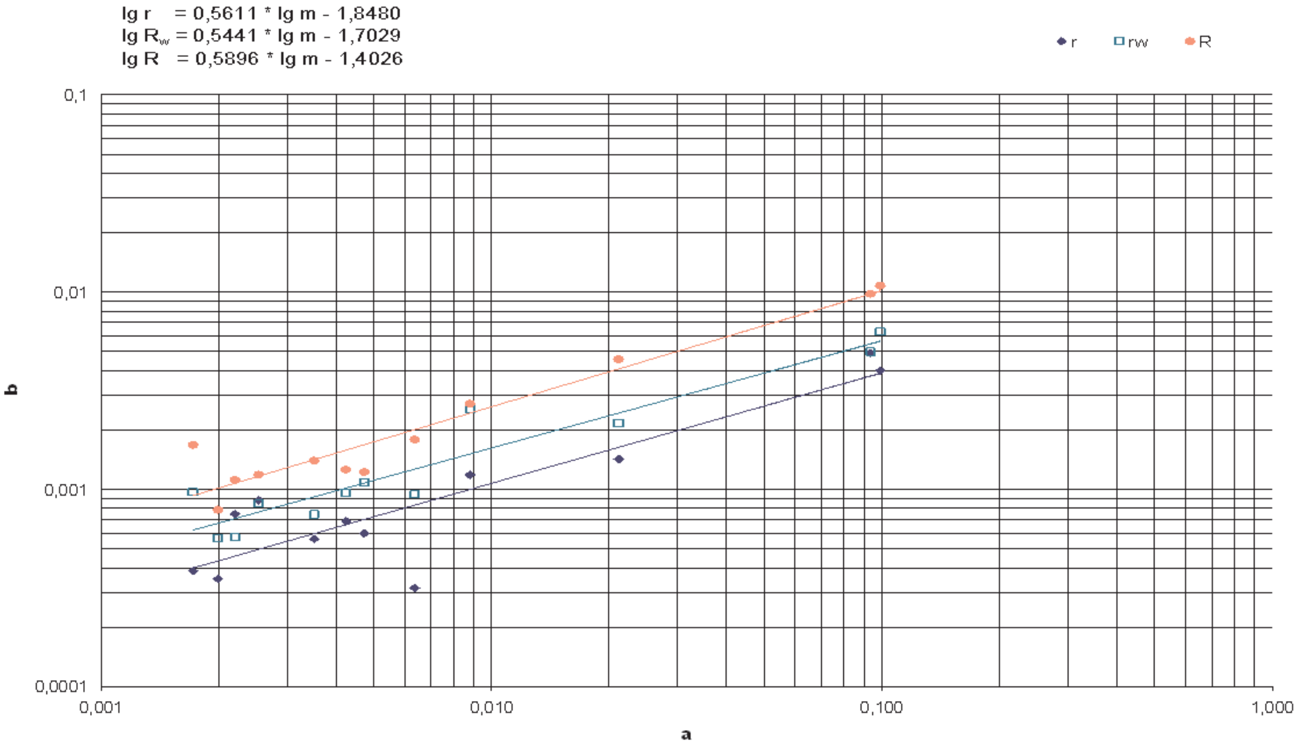


Key

a Al$_{(total)}$ content % (m/m)

b Precision (%)

Figure E.8 — Total aluminium



Key

a Sn content % (m/m)

b Precision (%)

Figure E.9 — Tin

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