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Chemical analysis of ferrous materials — Analysis of ferro-silicon — Determination of Al, Ti and P by inductively coupled plasma optical emission spectrometry

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National foreword

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Analyse chimique des matériaux ferreux - Analyse du ferro-silicium - Détermination de Al, Ti et P par spectrométrie d'émission optique avec source à plasma induit

Chemische Analyse von Ferrolegierungen - Analyse von Ferrosilizium - Bestimmung von Al, Ti und P durch induktiv gekoppeltes Plasma und optische Emissionsspektrometrie

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Contents

Foreword

This document (CEN/TR 10353:2011) 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

1 Scope

This Technical Report describes an inductively coupled plasma optical emission spectrometric method for the determination of Al, Ti and P contents in ferro-silicon materials.

The method is applicable to:

- Al contents between 0,2 and 2 %;
- Ti contents between 0,02 and 0,25 %;
- P contents between 0,005 and 0,05 %.

The procedure is valid for the analytical lines given in Table 1. This table also gives, for each line, the spectral interferences, which shall be corrected.

NOTE The interferences extent as well as other possible interferences depend on the temperature in the plasma and on the optical resolution of the spectrometer used.

Table 1 — Spectral lines recommended together with the interferences which shall be corrected

Element	Wavelength (nm)	Interferences
Al	308,22	V
Ti	337,28	V, Ni
P	178,29	Mo

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.

EN ISO 648, *Laboratory glassware — Single-volume pipettes (ISO 648:2008)*

EN ISO 1042, *Laboratory glassware — One-mark volumetric flasks (ISO 1042:1998)*

3 Principle

Dissolution of a test portion with nitric, hydrofluoric and perchloric acids. Addition of hydrochloric acid.

Filtration and ignition of the acid insoluble residue.

Fusion of the residue with sodium hydrogen sulphate, dissolution of the melt and addition of this solution to the reserved filtrate.

After suitable dilution and, if necessary, addition of an internal reference element, the solution is filtered and nebulised into an inductively coupled plasma optical emission spectrometer.

The intensity of the emitted light from each element is then measured (simultaneously with that emitted from the internal reference element, where relevant).

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 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.

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

4.3 Hydrochloric acid, solution 1 + 1

Add 500 ml of hydrochloric acid (4.2) to 500 ml of water.

4.4 Hydrochloric acid, solution 1 + 9

Add 50 ml of hydrochloric acid (4.2) to 450 ml of water.

4.5 Nitric acid, HNO_3 (ρ_{20} = 1,40 g/ml)

4.6 Perchloric acid, $HClO_4$ (ρ_{20} = 1,68 g/ml)

4.7 Sodium hydrogen sulphate

4.8 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.

4.9 Aluminium, 0,5 g/l standard solution

Weigh (0,5 ± 0,001) g of aluminium (99,98 % purity) and transfer into a 400 ml beaker. Add 50 ml of hydrochloric acid solution (4.3) and heat gently until aluminium is completely dissolved. After cooling, transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix well.

1 ml of this solution contains 0,5 mg of Al.

4.10 Titanium, 0,5 g/l standard solution

Weigh (0,5 ± 0,001) g of titanium (99,98 % purity) and transfer into a 400 ml beaker. Add 25 ml hydrochloric acid solution (4.3) and 5 to 10 drops of hydrofluoric acid (4.1). Heat gently until titanium is completely dissolved. After cooling, transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix well.

1 ml of this solution contains 0,5 mg of Ti.

4.11 Titanium, 0,05 g/l standard solution [freshly prepared]

Transfer 20 ml of titanium standard solution (4.10) into a 200 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

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

4.12 Phosphorus, 0,1 g/l standard solution [freshly prepared]

Weigh (0,4393 ± 0,001) g of dried potassium dihydrogen phosphate and transfer into a 250 ml beaker. Dissolve it with water. Transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix well.

1 ml of this solution contains 0,1 mg of P.

4.13 Phosphorus, 0,01 g/l standard solution [freshly prepared]

Transfer 20,0 ml of phosphorus standard solution (4.12) into a 200 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this solution contains 0,01 mg of P.

4.14 Scandium, 1 g/l solution

Weight (1,534 ± 0,001) g of scandium oxide, Sc_2O_3, (99,98 % purity) and transfer into a 600 ml beaker. Dissolve in 40 ml nitric acid (4.5). Transfer into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

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 Platinum crucibles and covers

5.2 Polytetrafluoroethylene (PTFE) beakers

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.

The spectrometer can be either of simultaneous or of sequential type. A sequential spectrometer can be equipped with an extra arrangement for simultaneous measurement of the internal reference element emitted light. In this case the sequential spectrometer can be used for the measurement method using the internal reference element. If the sequential spectrometer is not equipped with this arrangement, the internal reference element shall not be used.

6 Sampling

Sampling shall be carried out in accordance with appropriate international or national standards for ferro alloys.

7 Procedure

7.1 Preparation of the test solution

7.1.1 Test portion

Weigh, to the nearest 0,001 g, 0,5 g of the test sample.

7.1.2 Dissolution of the test portion

Transfer the test portion (7.1.1) into a platinum crucible (5.1) having a suitable capacity or into a polytetrafluoroethylene (PTFE) beaker (5.2).

Add 10 ml of nitric acid (4.5) and, in small portions, 10 ml of hydrofluoric acid (4.1). After each addition swirl the crucible or the beaker and allow the reaction to subside. Then heat to complete the dissolution.

NOTE If the internal reference element is not used, care must be taken in order to avoid uncontrolled evaporation of the acids, since differences in acid concentrations in the different solutions will give interference. A way to homogenise the residual acid concentration is the evaporation of the sample solution to dryness, followed by the dissolution of the salts.

Add 2,5 ml of perchloric acid (4.6) and heat until copious white fumes appear. Cool, rinse the sides of the crucible or that of the beaker with water and swirl to dissolve the salts. Repeat the heating to copious fumes.

Cool and add 15 ml of hydrochloric acid (4.4). Heat gently, in order to dissolve all salts. Filter the solution through a close texture filter paper, collect the filtrate into a 250 ml beaker and rinse the crucible or the PTFE beaker and the filter with hot water. Reserve the filtrate.

Transfer the filter into a platinum crucible (5.1), dry at about 105 °C and then heat at about 600 °C to remove organic matter. Ignite at 1 000 °C, to remove volatile oxides, for 15 min.

Cool, add 0,5 g of sodium hydrogen sulphate (4.7) and melt. Cool and dissolve the fusion products with the minimum quantity of water. Add this solution quantitatively to the filtrate in the 250 ml beaker.

Transfer the solution quantitatively into a 100 ml volumetric flask. If the internal reference element is used add, with a calibrated pipette, 0,5 ml of the scandium solution (4.14).

Make up to the mark with water and mix well.

7.2 Preparation of the calibration solutions

7.2.1 Aluminium: calibration solutions

Transfer 0,15 g of pure iron (4.8) in each of a series of six 400 ml beakers and dissolve with 10 ml of nitric acid (4.5).

NOTE The iron amount (0,15 g) corresponds to a test portion of a ferro-silicon having a 30-70 % average composition.

After dissolution add 2,5 ml of perchloric acid (4.6) and evaporate to copious fumes. After cooling at room temperature, add 15 ml of hydrochloric acid (4.4) and heat gently, in order to dissolve the salts. Add 0,5 g of sodium hydrogen sulphate (4.7) and swirl to dissolve this reagent.

With calibrated pipettes, add the volumes of the aluminium standard solution (4.9) shown in Table 2.

Transfer each solution quantitatively into a series of 100 ml volumetric flasks. If the internal reference element is used add, with a calibrated pipette, 0,5 ml of the scandium solution (4.14).

Dilute to the mark with water and mix well.

Table 2 — Composition of the calibration solutions for aluminium

Calibration solution label	Aluminium standard solution volumes (4.9) (ml)	Corresponding aluminium mass (mg)	Corresponding aluminium content in the sample (%)
0	0	0	0
1	2	1,0	0,2
2	4	2,0	0,4
3	7	3,5	0,7
4	10	5,0	1,0
5	20	10,0	2,0

7.2.2 Titanium: calibration solutions

Proceed as specified in 7.2.1 from "Transfer 0,15 g of pure iron…" until "…and swirl to dissolve the salts."

With calibrated pipettes, add the volumes of the titanium standard solutions (4.10 or 4.11) shown in Table 3.

Transfer each solution quantitatively into a series of 100 ml volumetric flasks. If the internal reference element is used add, with a calibrated pipette, 0,5 ml of the scandium solution (4.14).

Dilute to the mark with water and mix well.

Table 3 — Composition of the calibration solutions for titanium

Calibration solution label	Titanium standard solutions volumes (4.10 or 4.11) (ml)	Corresponding titanium mass (mg)	Corresponding titanium content in the sample (%)
0	0	0	0
1	2,0 (4.11)	0,10	0,02
2	5,0 (4.11)	0,25	0,05
3	10,0 (4.11)	0,50	0,10
4	2,0 (4.10)	1,00	0,20
5	2,5 (4.10)	1,25	0,25

7.2.3 Phosphorus: calibration solutions

Proceed as specified in 7.2.1 from "Transfer 0,15 g of pure iron…" until "…and swirl to dissolve the salts."

With calibrated pipettes, add the volumes of the phosphorus standard solutions (4.12 or 4.13) shown in Table 4.

Transfer each solution quantitatively into a series of 100 ml volumetric flasks. If the internal reference element is used add, with a calibrated pipette, 0,5 ml of the scandium solution (4.14).

Dilute to the mark with water and mix well.

Table 4 — Composition of the calibration solutions for phosphorus

Calibration solution label	Phosphorus standard solutions volumes (4.12 or 4.13) (ml)	Corresponding phosphorus mass (mg)	Corresponding phosphorus content in the sample (%)
0	0	0	0
1	2,5 (4.13)	0,025	0,005
2	5,0 (4.13)	0,050	0,010
3	10,0 (4.13)	0,100	0,020
4	15,0 (4.13)	0,150	0,030
5	2,5 (4.12)	0,250	0,050

7.2.4 Multi-elemental calibration solutions (Al, Ti and P)

Proceed as specified in 7.2.1 from "Transfer 0,15 g of pure iron…" until "…and swirl to dissolve the salts."

With calibrated pipettes, add the volumes of the aluminium, titanium and phosphorus standard solutions (4.9, 4.10 or 4.11 and 4.12 or 4.13) shown in Table 5.

Transfer each solution quantitatively into a series of 100 ml volumetric flasks. If the internal reference element is used add, with a calibrated pipette, 0,5 ml of the scandium solution (4.14).

Dilute to the mark with water and mix well.

NOTE In this way any possible matrix effect will be minimized.

Table 5 — Composition of the multi-elemental calibration solutions (Al, Ti and P)

Calibration solution label	Aluminium standard solution volumes (4.9) (ml)	Titanium standard solution volumes (4.10) (ml)	Titanium standard solution volumes (4.11) (ml)	Phosphorus standard solution volumes (4.12) (ml)	Phosphorus standard solution volumes (4.13) (ml)
0	0	0	0	0	0
1	20 [2,0 %]	---	2,0 [0,02 %]	---	15,0 [0,030 %]
2	10 [1,0 %]	---	5,0 [0,05 %]	2,5 [0,05 %]	---
3	7 [0,7 %]	---	10,0 [0,10 %]	---	5,0 [0,010 %]
4	4 [0,4 %]	2,0 [0,20 %]	---	---	2,5 [0,005 %]
5	2 [0,2 %]	2,5 [0,25 %]	---	---	10,0 [0,020 %]

7.3 Spectrometric measurements

7.3.1 Adjustment of the apparatus

Start the inductively coupled plasma optical emission spectrometer (5.3) 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 1, 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.

NOTE 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.

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.

If the internal reference element (scandium in this case) is used, prepare the software to calculate the ratio between the intensity of each analyte and the scandium intensity.

The intensity of the internal reference element shall be measured simultaneously with that of the analyte intensity.

7.3.2 Spectrometric measurements of the calibration solutions

Carry out the spectrometric measurements of the calibration solutions (7.2.1, 7.2.2, 7.2.3 or 7.2.4). It is recommended to use a simultaneous spectrometer for measurements using "internal reference element" (ratio mode) (see 5.3).

For each calibration solution, carry out three to five integrations and calculate the corresponding mean intensity or mean ratioed intensity.

Establish the calibration curves using the measured mean intensities or the 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 possible discrepancies within the 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.

7.3.3 Spectrometric measurements of the test solutions

If necessary, filter the test solutions through a medium paper filter. Discard the first 2 to 3 millilitres.

Start each analytical series by a calibration of the instrument (see 7.3.2). 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) test solution, prepared as described in 7.1.

Check the results: the calibration will be accepted if all the results for the CRM (or IRM) 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 calibration procedure.

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

Start the measurements of the unknown samples.

Measure the drift control test solution (CRM 1 or IRM 1) at least once for every five unknown test solutions. Maximum drifts allowed are given in Table 6.

Table 6 — Drift survey

Element	Concentration range (%)	Maximum drift (%)
all	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

If abnormal deviations appear, reject the results concerned and restart the procedures described in 7.3.2 and 7.3.3.

Re-measuring CRM 1 or IRM 1 test solutions should be carried out before ending each analytical series measurements.

NOTE To achieve a better accuracy of the determinations, it's also advisable to carry out the measurements by bracketing the test solutions with the most suitable calibration solutions.

8 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.

9 Precision

Four laboratories in two European countries participated in an inter laboratory test programme under the auspices of ECISS/TC 102/WG 5, involving three determinations of Al, Ti and P at several levels.

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.

Details on the samples used are given in Annex B and the results obtained are reported in Annex C.

The sets of data available were too few for a statistical evaluation based on ISO 5725-2 and 5725-3. Only Mandel’s h and k statistics were used (see Figures C.1 to C.6) rather for illustrative purposes.

A short explanation on the suitability of the data presented is also given in Annex C.

10 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 Technical Report 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 Minimum practical resolution of the sequential spectrometer

A.1.1 Introduction

The practical assessment of the resolution normally involves a wavelength scan across the spectral line of interest, plotting the profile, measuring the "Full Width at Half Maximum" of the line and then calculating the resolution (to be expressed in nanometre). An example is shown in Figure A.1.

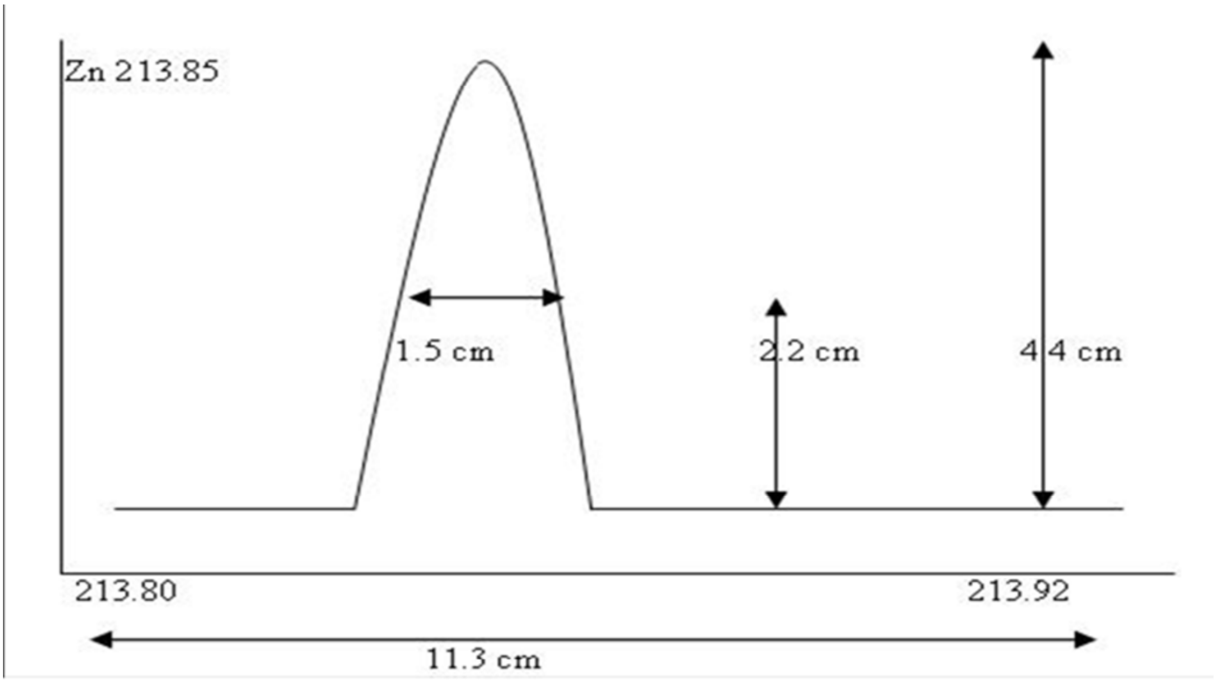

Figure A.1 — Example of the calculation of the practical resolution

A.1.2 Procedure

Calculate the bandwidth for each wavelength which shall be used including the one for the internal reference element (scandium in the case of the present method). The bandwidths shall be less than 0,030 nm.

A.2 Minimum short term precision

Calculate the standard deviation of 10 consecutive measurements of the absolute or ratioed intensity of the emitted light of the most concentrated calibration solution for each element. The relative standard deviation shall not exceed 0,4 % of the mean absolute or ratioed intensities.

A.3 Minimum long term precision

Calculate the standard deviation of 7 mean values of 3 measurements of the absolute or ratioed intensity of the emitted light of the most concentrated calibration solution for each element. Each set of measurements shall be carried out every half an hour during a total time of 3 h. The relative standard deviation shall not exceed 1,0 % of the absolute mean intensities or 0,6 % of the mean ratioed intensities.

A.4 Background equivalent concentration and limit of detection

A.4.1 General

Prepare three solutions containing the analyte elements of interest at concentration levels of zero ("blank"), 10 times and 1 000 times the expected limit of detection. These solutions should also have acids concentrations similar to those of the test solutions to be analysed.

Nebulise the 1 000 x DL solution and wait about ten seconds after the solution arrives in the plasma to ensure stable nebulisation. Optimise the operating and instrumental conditions for the element under consideration and set to 3 seconds the integration time.

NOTE 3 s integration time is valid for conventional spectrometers equipped with photomultipliers. Other integration times can be selected. Follow the manufactures recommendation.

A.4.2 Determination of the limit of detection

Nebulise the blank solution for approximately ten seconds and then take ten readings at the pre selected integration time.

Nebulise the "10 times limit of detection solution" for approximately ten seconds and then take ten readings at the pre selected integration time.

From the intensity readings obtained for the blank and the "10 times limit of detection" solutions, calculate the corresponding mean intensities X_b and X_{10} and the standard deviation of the blank S_b.

Taking into account the statistical risks α and β each of them at the 95 % level, the limit of detection (DL) is calculated according to the equation:

$$\mathrm{DL} = \frac{4{,}65 \times S_b \times C_{10}}{X_{10} - X_b}$$

where

C_{10} is the concentration of the "10 times limit of detection" solution in mg/l.

It should be pointed out that the detection limits calculated in this way have a wide margin of error due to the limited number of replicate measurements.

A.4.3 Determination of the background equivalent concentration (BEC)

Calculate the background equivalent concentration (BEC) according to the expression.

$$\mathrm{BEC} = \frac{X_b}{X_{10} - X_b} \times C_{10}$$

A.5 Spectral interferences

A.5.1 General

Spectral interferences will give a higher intensity than would be expected leading to too high results. Interferences can be quantified by calculating the apparent concentration of the analyte given by a certain amount of interfering element.

For each analytical line, calculate the apparent spectral interferences as follows:

Measure the absolute intensity of the analyte line while nebulising water and a 1 mg/l solution of the analyte under consideration. Subtract the intensity corresponding to water in order to obtain the net reading intensity of the analyte I_N.

Measure the absolute intensity on the analyte line while nebulising a 1 000 mg/l solution of the possible interfering element and subtract the intensity for water. This will give the net interfering intensity I_{IN}.

Calculate the apparent concentration C_A in mg/l of the analyte for a concentration of 1 mg/l of the interfering element, as:

$$C_A = \frac{I_{IN}}{I_N \text{ x } 1000}$$

If the interferences are less than 0,005 mg/l no corrections have to be applied.

A.6 Linearity of the calibration curves

The linearity of the calibration curves is checked by calculating the correlation coefficient, CC.

This coefficient should be, at least, 0,999.

Annex B
(informative)

Test samples used for the precision test

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

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

Sample label	Al (%)	Ti (%)	P (%)	Si (%)	Fe (%)	B (%)
NBS 59 A	0,35		0,016	48,1	50,0	0,058
DL 2307	6,01	0,073	0,020	55,9	12,6	
NBS 58 A	0,95	0,051	0,009	73,2	25,2	0,001
IPT 56	0,31	0,020	0,022	75,0	24,1	
ECRM 582-2	1,15	0,225	0,018	75,2	21,4	0,005
JSS 720-4	1,52		0,032	76,4		
ECRM 529-1	0,86	0,090	0,032	91,1	6,2	

Annex C
(informative)

Detailed results obtained from the precision test

C.1 Aluminium results

C.1.1 Results

Table C.1 — Aluminium

		NBS 59 A		DL 2307		NBS 58 A		IPT 56	
		Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
LAB 3	Individual values	0,340 7	0,340 7	5,604 4	5,531 3	0,940 8	0,940 8	0,315 5	0,309 6
		0,344 4		5,607 8		0,941 9		0,315 6	
	Laboratory mean	0,352 3		***5,581 2***		0,941 2		0,313 6	
LAB 4	Individual values	0,344 0	0,344 0	5,961 1	5,939 0	0,972 9	0,966 4	0,318 7	0,322 0
		0,347 2		5,837 0		0,976 0		0,307 4	
	Laboratory mean	0,346 2		5,912 4		0,971 8		0,316 0	
LAB 5	Individual values	0,350 1	0,350 1	5,936 6	5,922 1	0,936 7	0,937 8	0,291 6	0,293 2
		0,354 6		5,889 9		0,936 7		0,293 2	
	Laboratory mean	0,352 0		5,916 2		0,937 1		0,292 7	
LAB 6	Individual values	0,340 8	0,340 8	5,414 2	5,532 0	0,932 6	0,842 3	0,311 5	0,297 2
		0,327 0		5,512 3		0,883 3		0,299 8	
	Laboratory mean	0,342 7		***5,486 2***		***0,886 1***		0,302 8	
	Mean value (%)	0,348 3		5,724 0		0,934 0		0,306 3	
	Standard deviation (%)	0,004 7		0,223 2		0,035 5		0,010 7	
	RSD (%)	1,35		3,90		3,80		3,49	
	Certified value (%)	0,35		6,01		0,95		0,31	

Table C.1 — Aluminium *(continued)*

		ECRM 582-2		JSS 720-4		ECRM 529-1	
		Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
LAB 3	Individual values	1,206 0	1,196 6	1,510 2	1,469 3	0,904 1	0,881 0
		1,197 2		1,481 2		0,900 1	
	Laboratory mean	1,199 9		1,486 9		0,895 1	
LAB 4	Individual values	1,217 4	1,175 7	1,530 1	1,522 5	0,900 7	0,917 2
		1,211 8		1,521 9		0,875 5	
	Laboratory mean	1,201 6		1,524 8		0,897 8	
LAB 5	Individual values	1,181 7	1,187 0	1,465 4	1,477 7	0,879 8	0,867 4
		1,176 6		1,492 8		0,867 3	
	Laboratory mean	1,181 8		1,478 6		0,871 5	
LAB 6	Individual values	1,120 5	1,032 4	1,420 7	1,282 5	0,870 1	0,876 4
		1,032 7		1,377 0		0,923 6	
	Laboratory mean	***1,061 9***		***1,360 1***		0,890 0	

	ECRM 582-2	JSS 720-4	ECRM 529-1
Mean value (%)	1,161 3	1,462 6	0,888 6
Standard deviation (%)	0,066 9	0,071 3	0,011 8
RSD (%)	5,76	4,87	1,33
Certified value (%)	1,15	1,52	0,86

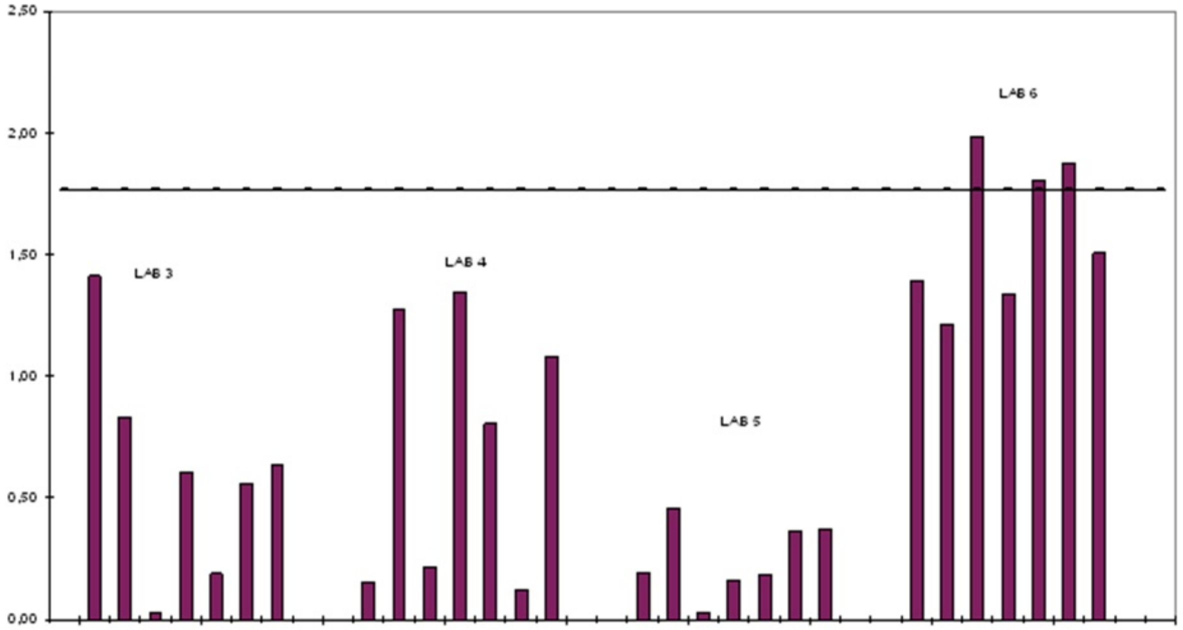

Figure C.1 — Aluminium - Mendel's k test for intra laboratory consistency (99 % confidence level)

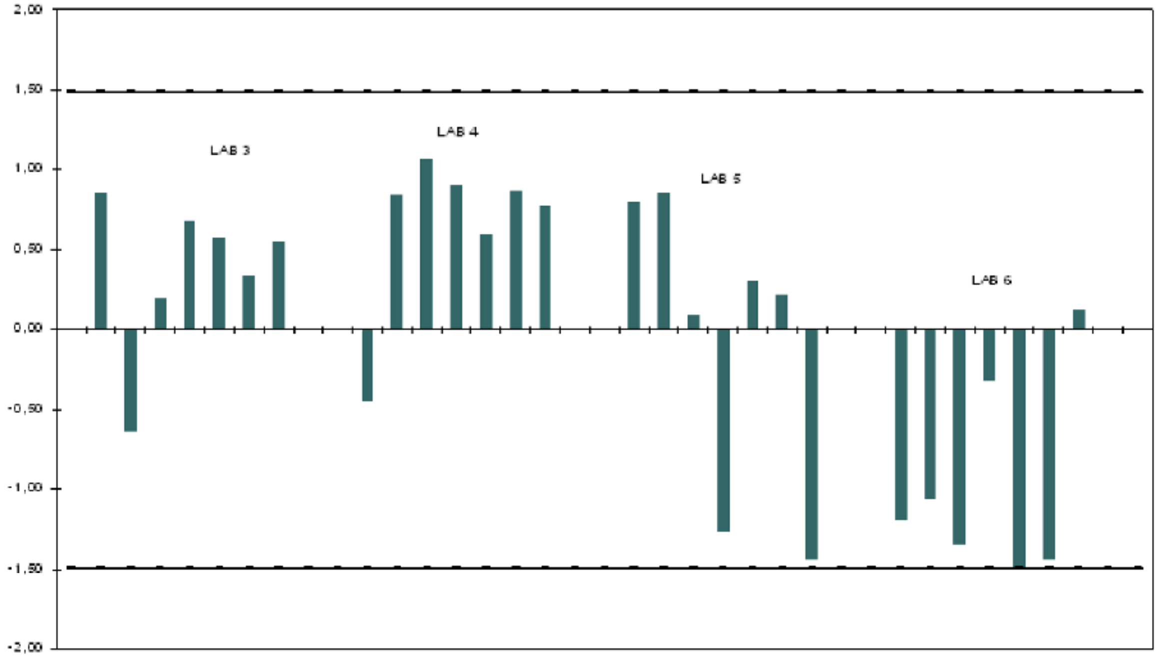

Figure C.2 — Aluminium — Mendel's h test for between laboratory consistency (99 % confidence level)

C.1.2 Comments on the suitability of the data for aluminium

On the basis of the data shown in Table C.1 and on the Mendel's statistics from Figures C.1 and C.2, the results from "Lab 6" show discrepancies when compared to the three other sets: they have a wide spread (even "abnormal" for three samples) and most of them have a quite important low tendency level.

However, no removal of these rather doubtful data was carried out, taking into account the reduced size of the population under concern.

Nevertheless, the mean values of the individual means of the other three laboratories are in a sufficiently good agreement with the "referee values" of the samples used, except for sample DL 2307.

This sample DL 2307 has an aluminium content (~ 6 %) that is out of the scope of the method proposed (0,01 % to 5 %) for the precision test. The results got for this sample by the different laboratories might therefore have been obtained "by extrapolation".

Consequently, the scope of the present Technical Report was reduced to the range from 0,2 % to 2 %.

C.2 Titanium results

C.2.1 Results

Table C.2 — Titanium

		DL 2307		NBS 58 A		IPT 56	
		Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
LAB 3	Individual values	0,060 9	0,059 7	0,045 3	0,045 3	0,014 6	0,015 4
		0,061 5		0,044 9		0,015 7	
	Laboratory mean	***0,060 7***		***0,045 2***		***0,015 2***	
LAB 4	Individual values	0,068 2	0,072 3	0,052 1	0,055 1	0,021 8	0,021 2
		0,064 9		0,049 9		0,021 2	
	Laboratory mean	0,068 5		0,052 4		0,021 4	
LAB 5	Individual values	0,069 3	0,069 0	0,049 0	0,049 3	0,019 5	0,019 4
		0,068 7		0,049 3		0,019 5	
	Laboratory mean	0,069 0		0,049 2		0,019 5	
LAB 6	Individual values	0,064 0	0,068 9	0,049 5	0,051 3	0,022 1	0,020 4
		0,070 0		0,049 9		0,020 9	
	Laboratory mean	0,067 6		0,050 2		0,021 1	

Mean value (%)	0,066 5	0,049 2	0,019 3
Standard deviation (%)	0,003 9	0,003 0	0,002 8
RSD (%)	5,68	6,10	14,5
Certified value (%)	0,073	0,051	0,02

Table C.2 — Titanium *(continued)*

		ECRM 582-2		ECRM 529-1	
		Day 1	Day 2	Day 1	Day 2
LAB 3	Individual values	0,235 0	0,229 0	0,093 7	0,092 2
		0,230 4		0,093 1	
	Laboratory mean	0,231 5		0,093 0	
LAB 4	Individual values	0,235 6	0,223 3	0,098 9	0,092 2
		0,229 2		0,096 9	
	Laboratory mean	0,229 4		0,096 0	
LAB 5	Individual values	0,227 0	0,226 7	0,093 9	0,092 1
		0,225 4		0,092 6	
	Laboratory mean	0,226 4		0,092 9	
LAB 6	Individual values	0,227 2	0,203 0	0,123 7	0,108 2
		0,199 7		0,113 4	
	Laboratory mean	0,210 0		***0,115 1***	

	ECRM 582-2	ECRM 529-1
Mean value (%)	0,224 3	0,099 2
Standard deviation (%)	0,009 8	0,010 7
RSD (%)	4,37	10,8
Certified value (%)	0,225	0,09

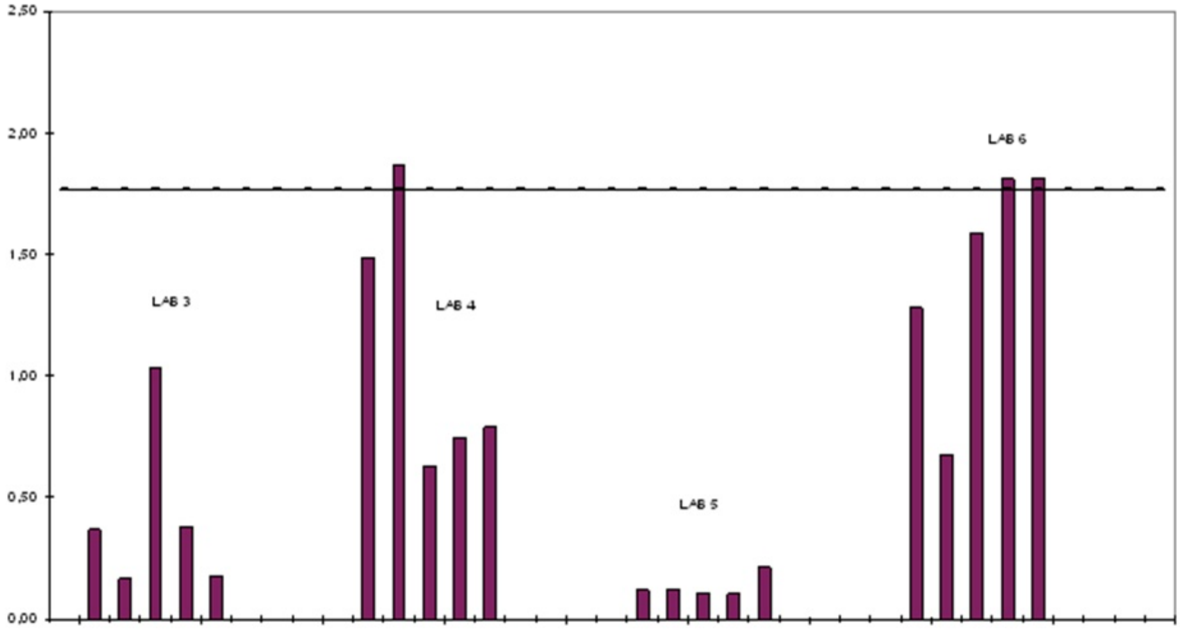

Figure C.3 — Titanium — Mendel's k test for intra laboratory consistency (99 % confidence level)

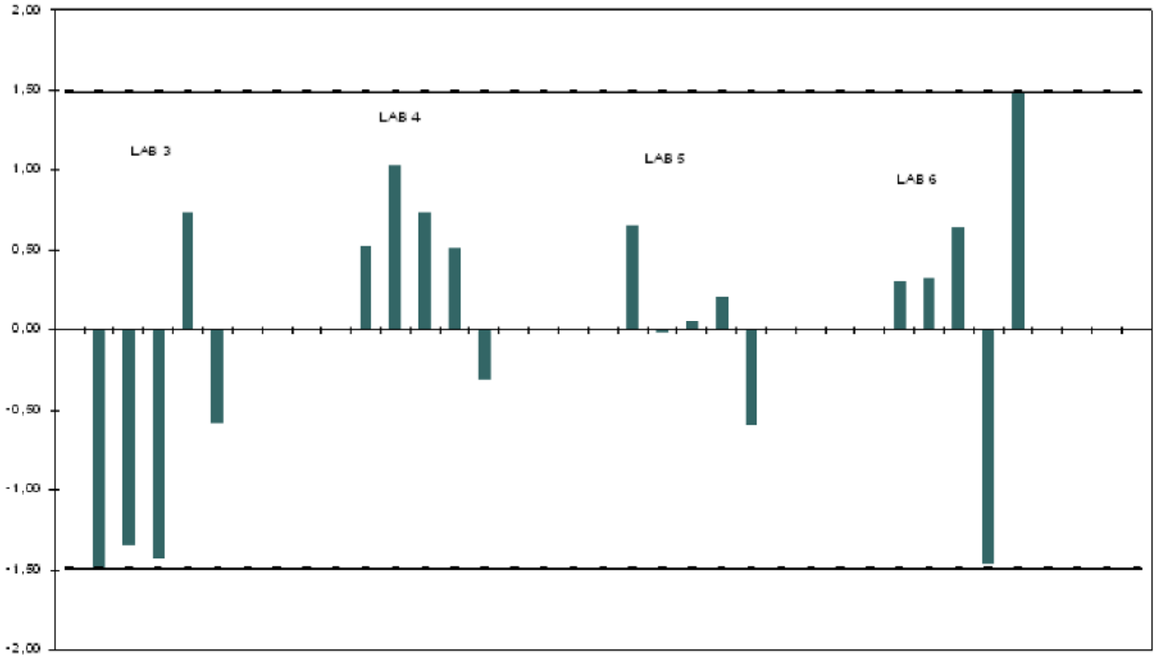

Figure C.4 — Titanium — Mendel's h test for between laboratory consistency (99 % confidence level)

C.2.2 Comments on the suitability of the data for titanium

On the basis of the data shown in Table C.2 and on the Mendel's statistics from Figures C.3 and C.4, the results from "Lab 3" show some discrepancies when compared to the three other sets: data below 0,09 % have a quite important low tendency level. Also, "Lab 6" has provided a quite high result for the ECRM 529-1 sample.

However, no removal of these rather doubtful data was carried out, taking into account the reduced size of the population under concern.

In spite of the four "inaccurate" results, the trueness of the other individual mean values is acceptable, within the range 0,02 % to 0,25 %.

C.3 Phosphorus results

C.3.1 Results

Table C.3 — Phosphorus

		NBS 59A		DL 2307		NBS 58 A	
		Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
LAB 3	Individual values	0,020 1	0,019 6	0,022 8	0,021 5	0,009 5	0,009 5
		0,019 9		0,025 2		0,010 8	
	Laboratory mean	0,019 9		0,023 2		0,009 9	
LAB 4	Individual values	0,015 1	0,014 8	0,018 7	0,021 0	0,008 6	0,009 4
		0,016 5		0,018 3		0,008 7	
	Laboratory mean	0,015 4		0,019 3		0,008 9	
LAB 5	Individual values	0,019 3	0,019 6	0,018 5	0,018 9	0,006 2	0,006 3
		0,020 0		0,017 6		0,006 3	
	Laboratory mean	0,019 6		0,018 3		***0,006 3***	
LAB 6	Individual values	0,014 0	0,014 7	0,020 2	0,015 2	0,010 5	0,007 3
		0,013 5		0,014 8		0,007 8	
	Laboratory mean	0,014 1		0,016 7		0,008 5	

Mean value (%)	0,017 3	0,019 4	0,008 4
Standard deviation (%)	0,002 9	0,002 7	0,001 5
RSD (%)	16,7	13,9	17,9
Certified value (%)	0,016	0,02	0,009

Table C.3 — Phosphorus *(continued)*

		JSS 720-4		ECRM 529-1	
		Day 1	Day 2	Day 1	Day 2
LAB 3	Individual values	0,032 7	0,033 4	0,012 3	0,011 4
		0,033 4		0,011 1	
	Laboratory mean	0,033 2		0,011 6	
LAB 4	Individual values	0,032 7	0,031 8	0,013 2	0,013 1
		0,032 6		0,012 3	
	Laboratory mean	0,032 3		0,012 9	
LAB 5	Individual values	0,026 7	0,028 6	0,006 9	0,006 8
		0,028 6		0,006 6	
	Laboratory mean	0,028 0		***0,006 8***	
LAB 6	Individual values	0,028 0	0,030 6	0,015 0	0,012 8
		0,030 4		0,013 2	
	Laboratory mean	0,029 7		0,013 7	

Mean value (%)	0,030 8	0,011 2
Standard deviation (%)	0,002 4	0,003 1
RSD (%)	7,79	27,7
Certified value (%)	0,032	0,013

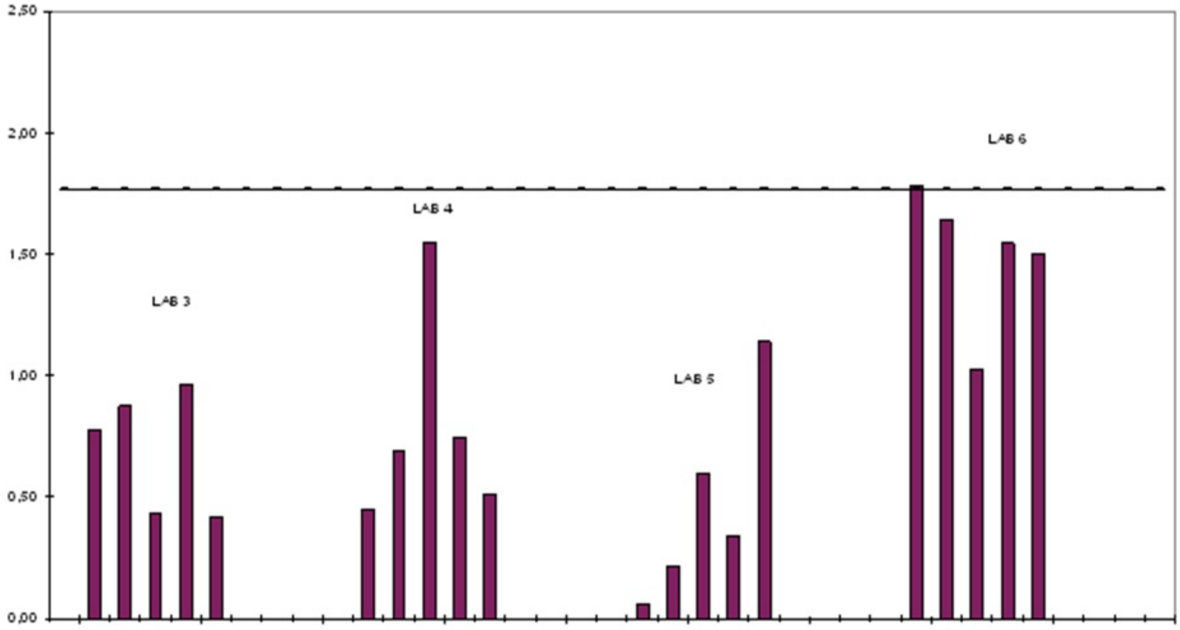

Figure C.5 — Phosphorus — Mendel's test for intra laboratory consistency (99 % confidence level)

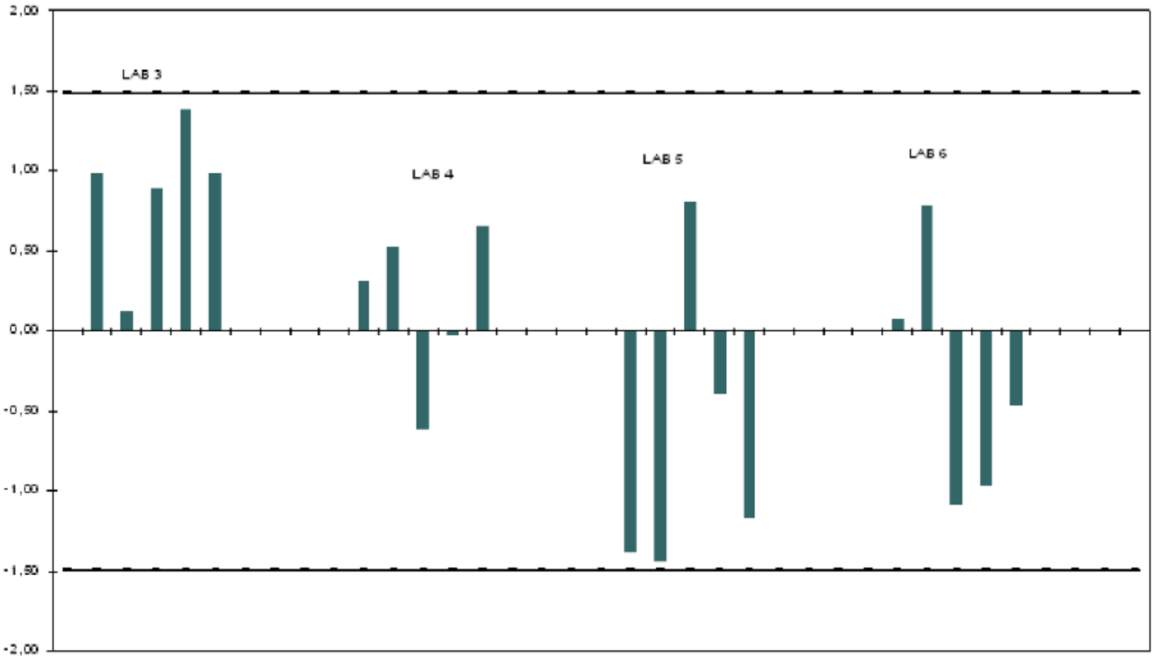

Figure C.6 — Phosphorus — Mendel's h test for between laboratory consistency (99 % confidence level)

C.3.2 Comments on the suitability of the data for phosphorus

On the basis of the data shown in Table C.3 and on the Mendel's statistics from Figures C.5 and C.6, the main discrepancies are two low tendency results from "Lab 5" and a general wide spread related to results from "Lab 6".

However, no removal of these rather doubtful data was carried out, taking into account the reduced size of the population under concern.

The trueness of the raw mean values being acceptable within the range 0,005 % to 0,05 %, it was therefore assumed that the method is suitable enough for this specific determination.

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