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Analysis of steels and irons — Internal laboratory procedure for checking the accuracy of an analytical method by using Certified Reference Materials

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National foreword

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English Version

Analysis of steels and irons - Internal laboratory procedure for checking the accuracy of an analytical method by using Certified Reference Materials

Analyse des aciers et des fontes - Procédure de contrôle intralaboratoire de l'exactitude d'une méthode analytique au moyen de Matériaux de Référence Certifiés

Analyse von Stahl und Eisen - Laboratoriumsinternes Verfahren zur Überprüfung der Richtigkeit eines - Analysenverfahrens mit Hilfe zertifizierter Referenzmaterialien

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Contents

Foreword

This document (CEN/TR 10350:2013) has been prepared by Technical Committee ECISS/TC 102 “Methods of chemical analysis for iron and steel”, the secretariat of which is held by SIS.

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.

This document supersedes CEN/TR 10350:2009.

In comparison with the previous version of CEN/TR 10350, the following significant technical changes were made:

- Definition 3.12: Correction of the definition for “uncertainty of the certified values”;
- Table C.7: Correction of the confidence level for χ^2;
- C.2.3.3: Correction of the sample label: G instead of A.

Introduction

This Technical Report defines a procedure for checking, in each specific laboratory, the accuracy of an analytical method by the application of statistical principles to the analytical results obtained on Certified Reference Materials (CRMs).

This Technical Report is an adaptation of ISO Guide 33:2000 mostly for the specific cases where EURONORM-CRMs are used for checking, in an intralaboratory context, the accuracy of an analytical method.

Nevertheless, it may be adopted in any other case where CRMs selected have similar quality levels to those of EURONORM-CRMs.

1 Scope

The present statistical procedure describes how to check results for absence of bias by comparison of these analytical results with those obtained during the certification of CRMs.

If the resulting data confirm the absence of bias, the method may be considered accurate when applied to all steels and irons whose composition ranges are adequately covered or bounded by the CRMs used.

The resulting data give also an estimate of the repeatability and/or the intermediate precision ("intralaboratory reproducibility") for the CRMs used. The comparison of these analytical data with the repeatability data obtained during the certification may also be performed depending on the strict purpose of the method under consideration.

For the purpose of this Technical Report, the use of existing CRMs is essential for the assessment of the trueness, but it may be only indicative for the other statistical data.

NOTE This Technical Report does not describe the use of CRMs as calibrants, this subject being treated in ISO Guide 32.

2 Principle

This Technical Report describes a procedure for checking an analytical method used in a specific laboratory by using data obtained from the analysis of CRMs.

The absence of bias ascertained with CRMs can be extended to the trueness of further analytical samples adequately covered or bounded by the selected CRMs. Nevertheless it should be underlined that this Technical Report is not appropriate for the assessment of the repeatability and/or the intermediate precision data of the further analytical samples to be tested by the analytical method under consideration.

Checking the trueness of an analytical method as applied by a specific laboratory involves the comparison of the mean value of the analytical results obtained by using CRMs with the certified value of each CRM selected. The standard deviation of the intralaboratory means of the selected CRMs is taken into account when making this comparison. Moreover, adjustment values chosen in advance by the laboratory, according to economic or technical limitations or stipulations are also taken into account.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
certified reference material
CRM
reference material characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability

NOTE 1 The concept of value includes qualitative attributes such as identity or sequence. Uncertainties for such attributes may be expressed as probabilities.

NOTE 2 Metrologically valid procedures for the production and certification of reference materials are given in, among others, ISO Guides 34 and 35.

NOTE 3 ISO Guide 31 gives guidance on the contents of certificates.

NOTE 4 VIM has an analogous definition (ISO/IEC Guide 99:2007, 5.14).

[SOURCE: ISO Guide 30; Amendment 1:2008]

3.2
reference material
RM

material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process

NOTE 1 RM is a generic term.

NOTE 2 Properties can be quantitative or qualitative, e.g. identity of substances or species.

NOTE 3 Uses may include the calibration of a measurement system, assessment of a measurement procedure, assigning values to other materials, and quality control.

NOTE 4 A single RM cannot be used for both calibration and validation of results in the same measurement procedure.

NOTE 5 VIM has an analogous definition (ISO/IEC Guide 99:2007, 5.13), but restricts the term “measurement” to apply to quantitative values and not to qualitative properties. However, NOTE 3 of ISO/IEC Guide 99:2007, 5.13, specifically includes the concept of qualitative attributes, called “nominal properties”.

[SOURCE: ISO Guide 30; Amendment 1:2008]

3.3
accuracy

closeness of agreement between a test result and the true value

NOTE 1 In practice, the accepted reference value is substituted for the true value.

NOTE 2 The term "accuracy", when applied to a set of test or measurement results, involves a combination of random components and common systematic error or bias component.

NOTE 3 Accuracy refers to a combination of trueness and precision.

[SOURCE: ISO 3534-2:2006, 3.3.1]

3.4
bias

difference between the expectation of a test result or a measurement result and a true value

NOTE 1 Bias is the total systematic error as contrasted to random error. There may be one or more systematic error components contributing to the bias. A larger systematic difference from the true value is reflected by a larger bias value.

NOTE 2 The bias of a measuring instrument is normally estimated by averaging the error of indication over an appropriate number of repeated measurements. The error of indication is the "indication of a measuring instrument minus a true value of the corresponding input quantity".

NOTE 3 In practice, the accepted reference value is substituted for the true value.

[SOURCE: ISO 3534-2:2006, 3.3.2]

3.5
precision

closeness of agreement between independent test/measurement results obtained under stipulated conditions

NOTE 1 Precision depends only on the distribution of random errors and does not relate to the true value or the specified value.

NOTE 2 The measure of precision is usually expressed in terms of imprecision and computed as a standard deviation of the test results or measurement results. Less precision is reflected by a larger standard deviation.

NOTE 3 Quantitative measures of precision depend critically on the stipulated conditions. Repeatability conditions and reproducibility conditions are particular sets of extreme stipulated conditions.

[SOURCE: ISO 3534-2:2006, 3.3.4]

3.6
repeatability

precision under repeatability conditions

[SOURCE: ISO 3434-2:2006, 3.3.5]

3.7
repeatability conditions

conditions where independent test/measurement results are obtained with the same method on identical test/measurement items in the same test or measuring facility by the same operator using the same equipment within short intervals of time

NOTE Repeatability conditions include:

a) the same measurement procedure or test procedure;

b) the same operator;

c) the same measuring or test equipment used under the same conditions;

d) the same location;

e) repetition over a short period of time.

[SOURCE: ISO 3434-2:2006, 3.3.6]

3.8
reproducibility

precision under reproducibility conditions

NOTE 1 Reproducibility can be expressed quantitatively in terms of the dispersion characteristics of the results.

NOTE 2 Results are usually understood to be corrected results.

NOTE 3 This definition is not used in the present document: it is given only to clarify the next item.

[SOURCE: ISO 3534-2:2006, 3.3.10]

3.9
reproducibility conditions

observation conditions where independent test/measurement results are obtained with the same method on identical test/measurement items in different test or measurement facilities with different operators using different equipment

[SOURCE: ISO 3534-2:2006, 3.3.11]

3.10
intermediate precision

precision under intermediate precision conditions

[SOURCE: ISO 3534-2:2006, 3.3.15]

3.11
intermediate precision conditions

conditions where test results or measurement results are obtained with the same method, on identical test/measurement items in the same test or measurement facility, under some different operating condition

NOTE 1 There are four elements to the operating condition: time, calibration, operator and equipment.

NOTE 2 A test house is an example of a test facility. A metrology laboratory is an example of a measurement facility.

[SOURCE: ISO 3534-2:2006, 3.3.16]

3.12
uncertainty of the certified values

in the particular case of EURONORM-CRMs, the uncertainty of each certified value is expressed as the 95 % half-width confidence interval "C(95 %)" of the mean of the intralaboratory means

Note 1 to entry: It is calculated from Formula (1):

$$C(95\,\%) = \frac{t \times S_M}{\sqrt{n}} \tag{1}$$

where

t is the Student's value at the desired probability with n-1 degrees of freedom;

S_M is the standard deviation of the intralaboratory means;

n is the number of acceptable intralaboratory mean values.

Note 2 to entry: This definition is not used in the present document: it is only given for clarification.

4 Procedure

4.1 General

The analytical method for the measurement shall be fixed, i.e. a written document shall exist laying down all the details. There shall be no changes to the method during the course of the experiment.

CRMs to be selected shall cover the range of the analytical method, which shall at least be bounded with low and high content, and if possible, shall include an intermediate content.

Furthermore, it should be possible to extend the choice of CRMs to cover similar matrices representing the compositions of the analytical samples intended to be analysed.

For example, if the analytical method concerns the determination of copper in low alloy steel samples with a nickel content of about 0,01 % and also in samples having a nickel content of about 1 % it is advisable to test the method within its full range for both kind of matrices.

4.2 Number of replicate determinations

The number of replicate determinations required, n_0, depends mainly on the values of α and β and the alternative hypothesis chosen for the assessment of the precision.

NOTE α is the significance level and β is the type II error probability.

Table 1 shows the relation between the degrees of freedom ν (where in this case $\nu = n - 1$) and the ratio of the within-laboratory standard deviation of the analytical method, σ_{W1}, and the required value of the within-laboratory standard deviation, σ_{W0}, for various values of β at $\alpha = 0{,}05$.

For example, for $n = 10$ the probability that the variance of the analytical results will pass the appropriate χ^2-test at $\alpha = 0{,}05$ is no more than 1 % when within-laboratory standard deviation, σ_{W1}, of the analytical method is equal or larger than 2,85 times the required value of σ_{W0}.

The user needs to establish, before the analysis, an appropriate level of acceptability with regard to the ratio of σ_{W1} to σ_{W0} (the null hypothesis) and also the probability of falsely accepting a method which has, in fact, unacceptable precision (β, which is also the type II error probability).

Assume therefore that a user has decided that a method is acceptable if the within laboratory standard deviation is not more than three times the certification standard deviation. This makes the null hypothesis $\sigma_{W1} \leq 3\,\sigma_{W0}$ and the alternative hypothesis $\sigma_{W1} > 3\,\sigma_{W0}$. Assume also that the user has decided that the acceptable probability of a false acceptance of the null hypothesis is 0,05 (or 5 %). From Table 1, reading down column 3 ($\beta = 0{,}05$), the first number less than 3 is 2,77. This corresponds to a ν of 6 (from column 1) and therefore the minimum number of replicate determinations required is $\nu + 1$, or 7. If the user had decided that the acceptable probability of a false acceptance of the same null hypothesis was 0,01 then a minimum of ten replicate determinations (ν of 9) would be required (reading from column 2 ($\beta = 0{,}01$)).

4.3 CRMs

The user should confirm the suitability of each CRM with respect to the certified value, its uncertainty, method(s) of characterisation, date of certification, statement of intended use, expiry date for unstable CRMs, packaging and storage conditions and special instructions for correct use given in the certificate and the size of test portion required for the measurement process.

4.4 Determinations

The user should perform independent replicate determinations. "Independent", in a practical sense, means that a replicate result is not influenced by previous replicate results. To perform replicate determinations means to repeat the whole procedure.

For example:

a) in the chemical analysis of a solid material, the procedure should be repeated from weighing of the test portion to the final reading or calculating of the result (taking aliquots from the same sample solution is not independent replication);

b) in spectrometric analysis:

    1) the whole process should be repeated for a solid sample, including grinding and surface finishing;

    2) the whole process should be repeated for powder samples from the test portion conditioning.

Independent replicate determinations can be achieved in several ways depending on the nature of the method. In some cases, however, parallel replication is not recommended because an error committed at any step of the procedure could affect all replicates.

The determination results could, if necessary, be scrutinised for possible outliers using the rules described in ISO 5725-2. It should be noted that an excessive number of suspected outliers indicates problems in the analytical method under consideration.

Table 1 — Ratio of the standard deviation of the measurement process to the required value for various values of *ß* and degrees of freedom ν at α = 0,05

ν	α = 0,05			
	ß **= 0,01**	***ß*** **= 0,05**	***ß*** **= 0,1**	***ß*** **= 0,5**
1	159,5	31,3	15,6	2,73
2	17,3	7,64	5,33	2,08
3	6,25	4,71	3,66	1,82
4	5,65	3,65	2,99	1,68
5	4,47	3,11	2,62	1,59
6	3,80	2,77	2,39	1,53
7	3,37	2,55	2,23	1,49
8	3,07	2,38	2,11	1,45
9	2,85	2,26	2,01	1,42
10	2,67	2,15	1,94	1,40
12	2,43	2,01	1,83	1,36
15	2,19	1,85	1,71	1,32
20	1,95	1,70	1,59	1,27
24	1,83	1,62	1,52	1,25
30	1,71	1,54	1,46	1,22
40	1,59	1,45	1,38	1,19
60	1,45	1,35	1,30	1,15
120	1,30	1,24	1,21	1,11

5 Evaluation of precision

5.1 Procedure

The required "precision" conditions are the repeatability (3.6) and/or whatever type of intermediate precision conditions (3.10).

The within laboratory precision of the analytical method is assessed by comparing the repeatability and/or whatever defined intermediate precision with the required value σ_{W0}.

Compute the average, $\overline{X}$, and the estimate of within-laboratory standard deviation, S_D:

$$\overline{X} = \sum_{i=1}^{n} \frac{X_i}{n} \tag{2}$$

$$S_D = \left[\sum_{i=1}^{n} \frac{(X_i - \overline{X})^2}{n-1} \right]^{1/2} \tag{3}$$

Compute the following ratio:

$$\chi_c^2 = \left(\frac{S_D}{\sigma_{W0}} \right)^2 \tag{4}$$

$\chi^2_{table} = \frac{\chi^2_{(n-1);\,0,95}}{n-1}$ = 0,95th quantile of the χ^2 distribution at degrees of freedom (n - 1) divided by the degrees of freedom (n - 1).

The table of the χ^2 distribution is presented in Annex B.

Decision:

$\chi^2_c \leq \chi^2_{table}$: There is no evidence that the measurement process is not as precise as required.

$\chi^2_c > \chi^2_{table}$: There is evidence that the measurement process is not as precise as required.

5.2 Evaluation

Calculate χ^2_c and χ^2_{table} as detailed above for all the CRMs tested.

If $\chi^2_c > \chi^2_{table}$ then:

a) ensure that the analytical method has been carried out according to the documented procedure;

b) investigate the possibility that the discrepancies are linked with the range and eventually define and test a new more limited range;

c) investigate the possibility that the discrepancies are linked to specific matrixes and then restrict the field of application to the relevant alloys.

6 Assessment of the trueness

6.1 Procedure

The trueness of the measurement process is checked by comparing the average $\overline{X}$ with the certified value μ considered as the true value.

There are two factors contributing to the difference between the certified value and the experimental results:

a) the standard deviation of the certified value (σ_L);

b) the standard deviation of the results of the analytical method under consideration (σ_D).

The following general condition is used as the criterion for acceptance:

$$\mu - a_2 - 2\sigma_L + 2\sigma_D \leq \overline{X} \leq \mu + a_1 + 2\sigma_L - 2\sigma_D \qquad (5)$$

where

a_1 and a_2	are adjustment values chosen in advance by the laboratory, according to economic or technical limitation or stipulation.

The standard deviation associated with the analytical method, σ_D, arises from the fact that the analytical procedure performed on the same material does not, in general, yield identical results every time it is applied. This fluctuation is attributed to unavoidable random errors inherent in every analytical method because the factors that may influence the outcome of a determination cannot all be completely controlled. This random fluctuation of the analytical results should be taken into account when assessing the trueness of the method.

The random fluctuation can be divided in two parts, but for the purpose of the present document, only the within laboratory or short term fluctuation, which has a mean of zero and a standard deviation of σ_{w1} is relevant; an estimate of σ_{w1} is given as S_D in Formula (3).Therefore, the condition (5) is expressed as:

$$\mu - a_2 - 2\sigma_L + 2S_D \leq \overline{X} \leq \mu + a_1 + 2\sigma_L - 2S_D \tag{6}$$

6.2 Assessment

If Formula (6) is not true for any of the CRMs analysed then:

a) ensure that the analytical method has been carried out according to the documented procedure;

b) investigate the possibility that the discrepancies are linked with the range and eventually define and test a new more limited range;

c) investigate the possibility that the discrepancies are linked to specific matrixes and then restrict the field of application to the relevant alloys.

7 Conclusion

The analytical method will be considered accurate under the conditions pre-defined by the laboratory, if the condition represented by the criterion (5) is respected for the whole set CRMs selected (after possible restrictions).

In all cases, the method documentation shall contain all of the data relating to these procedures.

This documentation shall include the decisions concerning any eventual restriction of the scope and/or the field of application of the method as well as a reference to this Technical Report.

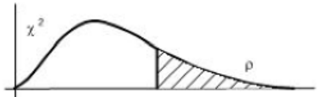
Annex A
(informative)

Symbols used

n_0	number of replicate results
α	significance level
β	type II error probability
ν	number of degrees of freedom
σ_{W1}	within-laboratory standard deviation
σ_{W0}	required value of the within laboratory standard deviation (expressed as s_w on the certificates of the EURONORM-CRMs)
$\overline{X}$	arithmetic mean of measurement results
S_D	estimate of within-laboratory standard deviation
x_i	individual result
n	number of results excluding outliers
μ	accepted reference value of a property (expressed as M_M on the certificates of the EURONORM-CRMs)
σ_D	standard deviation of the analytical method under consideration
a_1, a_2	adjustment values chosen in advance
σ_L	standard deviation of the certified value (expressed as s_M on the certificates of the EURONORM-CRMs)

Annex B
(informative)

Table of the χ^2 distribution



$\chi^2(n)$

n p	0,90	0,80	0,70	0,50	0,30	0,20	0,10	0,05	0,02	0,01
1	0,015 8	0,064 2	0,148	0,455	1,074	1,642	2,706	3,841	5,412	6,635
2	0,211	0,446	0,713	1,386	2,408	3,219	4,605	5,991	7,824	9,210
3	0,584	1,005	1,424	2,366	3,665	4,642	6,251	7,815	9,837	11,341
4	1,064	1,649	2,195	3,357	4,878	5,989	7,779	9,488	11,668	13,277
5	1,610	2,343	3,000	4,351	6,064	7,289	9,236	11,070	13,388	15,086
6	2,204	3,070	3,828	5,348	7,231	8,558	10,645	12,592	15,033	16,812
7	2,833	3,822	4,671	6,346	8,383	9,803	12,017	14,067	16,622	18,475
8	3,490	4,594	5,527	7,344	9,524	11,030	13,362	15,507	18,168	20,090
9	4,168	5,380	6,393	8,343	10,656	12,242	14,684	16,919	19,679	21,666
10	4,865	6,179	7,267	9,342	11,781	13,442	15,987	18,307	21,161	23,209
11	5,578	6,989	8,148	10,341	12,899	14,631	17,275	19,675	22,618	24,725
12	6,304	7,807	9,034	11,340	14,011	15,812	18,549	21,026	24,054	26,217
13	7,042	8,634	9,926	12,340	15,119	16,985	19,812	22,362	25,472	27,688
14	7,790	9,467	10,821	13,339	16,222	18,151	21,064	23,685	26,873	29,141
15	8,547	10,307	11,721	14,339	17,322	19,311	22,307	24,996	28,259	30,578
16	9,312	11,152	12,624	15,338	18,418	20,465	23,542	26,296	29,633	32,000
17	10,085	12,002	13,531	16,338	19,511	21,615	24,769	27,587	30,995	33,409
18	10,865	12,857	14,440	17,338	20,601	22,760	25,989	28,869	32,346	34,805
19	11,651	13,716	15,352	18,338	21,689	23,900	27,204	30,144	33,687	36,191
20	12,443	14,578	16,266	19,337	22,775	25,038	28,412	31,410	35,020	37,566
21	13,240	15,445	17,182	20,337	23,858	26,171	29,615	32,671	36,343	38,932
22	14,041	16,314	18,101	21,337	24,939	27,301	30,813	33,924	37,659	40,289
23	14,848	17,187	19,021	22,337	26,018	28,429	32,007	35,172	38,968	41,638
24	15,659	18,062	19,943	23,337	27,096	29,553	33,196	36,415	40,270	42,980
25	16,473	18,940	20,867	24,337	28,172	30,675	34,382	37,652	41,566	44,314
26	17,292	19,820	21,792	25,336	29,246	31,795	35,563	38,885	42,856	45,642
27	18,114	20,703	22,719	26,336	30,319	32,912	36,741	40,113	44,140	46,963
28	18,939	21,588	23,647	27,336	31,391	34,027	37,916	41,337	45,419	48,278
29	19,768	22,475	24,577	28,366	32,461	35,139	39,087	42,557	46,693	49,588
30	20,599	23,364	25,508	29,336	33,530	36,250	40,256	43,773	47,962	50,892

Annex C
(informative)

Examples

C.1 Checking the accuracy of an atomic absorption spectrometric method for the determination of manganese in low alloy steels

C.1.1 Introduction

The laboratory has determined the scope of the method to be 0,01 % to 2,0 % manganese for low alloy steels, where the maximum concentration of the other elements does not exceed 0,2 % and also for steels containing around 1 % nickel.

The laboratory decided that four replicates would be acceptable and that the adjustment values a_2 and a_1 were both equal to zero.

C.1.2 Characteristics of the CRMs selected

Six CRMs were selected, three of them having nickel contents below 0,2 % (labelled A, B and C), the other having nickel contents of about 1 % (labelled D, E and F).

For manganese, the certificate information for each CRM is given in Table C.1.

Table C.1 — Certificate information for manganese

	A	B	C	D	E	F
μ	0,011 2	0,505 7	1,915 2	0,013 2	0,371 2	1,817 0
σ_{W0}	0,000 2	0,002 1	0,009 4	0,000 3	0,002 7	0,013 6
σ_{L}	0,000 6	0,008 4	0,023 0	0,000 6	0,006 8	0,028 3

C.1.3 Results

C.1.3.1 General

The individual data obtained as well as the corresponding mean value ($\overline{X}$) and the estimate of within-laboratory standard deviation (S_D) are given in Table C.2.

Table C.2 — Results for manganese

	A	B	C	D	E	F
Individual data	0,010 6	0,503 0	1,923 4	0,012 9	0,366 9	1,822 1
	0,011 0	0,502 3	1,894 3	0,013 1	0,376 0	1,832 0
	0,011 3	0,508 4	1,909 6	0,012 5	0,371 7	1,797 8
	0,010 7	0,507 5	1,927 5	0,013 6	0,367 9	1,784 3
$\overline{X}$	0,010 9	0,505 3	1,913 7	0,013 0	0,370 6	1,809 1
S_D	0,000 32	0,003 1	0,015 0	0,000 46	0,004 1	0,021 9

C.1.3.2 Evaluation of the precision

The relevant calculations are presented in Table C.3.

Table C.3 — Evaluation of the precision

	A	B	C	D	E	F
S_D/σ_{W0}	1,581 1	1,473 9	1,598 9	1,524 5	1,532 3	1,608 8
χ_c^2	2,500	2,172	2,557	2,324	2,348	2,588
$\chi^2_{3;\,0,95}/3$	7,815/3 = 2,605					

For the six CRMs the expression $\chi_c^2 \leq \chi_{table}^2$ is true. Therefore, it can be assumed that there is no evidence that the analytical method is not as precise as required.

C.1.3.3 Assessment of the trueness

The required calculations are presented in Table C.4.

Table C.4 — Assessment of the trueness

	A	B	C	D	E	F
$\mu - a_2 - 2\sigma_L + 2S_D$	0,010 6	0,495 1	1,899 3	0,012 9	0,365 9	1,804 2
$\overline{X}$	0,010 9	0,505 3	1,913 7	0,013 0	0,370 6	1,809 1
$\mu + a_1 + 2\sigma_L - 2S_D$	0,011 8	0,516 3	1,931 1	0,013 5	0,376 5	1,829 8
ASSESSMENT	**YES**	**YES**	**YES**	**YES**	**YES**	**YES**

The condition "$\mu - a_2 - 2\sigma_L + 2S_D \leq \overline{X} \leq \mu + a_1 + 2\sigma_L - 2S_D$" is true in all cases. Thus, the method is as unbiased as required within the preselected scope and is suitable for both matrices for which it has been tested.

C.2 Checking the accuracy of an inductively coupled plasma optical emission spectrometric method for the determination of aluminium in low alloy steels

C.2.1 Introduction

The laboratory has determined the scope of the method to be 0,002 % to 0,05 % aluminium for low alloy steels, where the maximum concentration of the other elements does not exceed 0,2 %.

The laboratory decided that six replicates would be acceptable and that the adjustment values a_2 and a_1 were both equal to 0,000 3.

C.2.2 Characteristics of the CRMs selected

Three CRMs (labelled G, H and I) were selected and the certificate information regarding their aluminium content is given in Table C.5.

Table C.5 — Certificate information for aluminium

	G	H	I
μ	0,002 40	0,009 3	0,047 8
σ_{W0}	0,000 30	0,000 5	0,001 0
σ_{L}	0,000 55	0,001 1	0,003 1

C.2.3 Results

C.2.3.1 General

The individual data obtained as well as the corresponding mean value ($\overline{X}$) and the estimate of within-laboratory standard deviation (S_D) are given in Table C.6.

Table C.6 — Results for aluminium

	G	H	I
Individual data	0,002 0	0,008 1	0,049 8
	0,001 5	0,009 6	0,047 6
	0,002 4	0,008 4	0,048 8
	0,002 6	0,009 4	0,045 6
	0,001 7	0,009 1	0,047 5
	0,003 1	0,009 9	0,048 4
$\overline{X}$	0,002 2	0,009 1	0,048 0
S_D	0,000 6	0,000 7	0,001 4

C.2.3.2 Evaluation of the precision

The relevant calculations are presented in Table C.7.

Table C.7 — Evaluation of the precision

	G	H	I
S_D/σ_{W0}	1,993 5	1,405 2	1,427 9
χ_c^2	3,974	1,975	2,039
$\chi^2_{5;\,0,95}/5$	11,070/5 = 2,214		

The condition $\chi_c^2 \leq \chi_{table}^2$ is NOT true for the low content level.

It should be assumed that the analytical method tested only presents the precision required for aluminium contents starting at 0,009 %.

It is still the case, even when the condition $\chi_c^2 \leq \chi_{table}^2$ is considered at the significance level of 0,99: $\chi^2_{5;\,0,99}/5$ = 3,017.

C.2.3.3 Assessment of the trueness

The required calculations are presented in Table C.8.

Table C.8 — Assessment of the trueness

	G	H	I
$\mu - a_2 - 2\sigma_L + 2S_D$	0,002 20	0,008 21	0,044 16
$\overline{X}$	0,002 22	0,009 08	0,047 95
$\mu + a_1 + 2\sigma_L - 2S_D$	0,002 60	0,010 39	0,051 44
ASSESSMENT	**YES**	**YES**	**YES**

Taking into account the bias limit defined as "acceptable" (0,000 3 %), the condition "$\mu - a_2 - 2\sigma_L + 2S_D \leq \overline{X} \leq \mu + a_1 + 2\sigma_L - 2S_D$" is true even in the case of sample G.

Nevertheless, the precision required was not reached for the lowest content level.

Therefore it is advisable to reduce the scope of the method from "0,002 to 0,05 %" to "0,009 to 0,05 %".

C.3 Checking the accuracy of a spark optical emission spectrometric method for the determination of vanadium in alloy steels

C.3.1 Introduction

The laboratory has determined the scope of the method to be 0,01 % to 0,20 % vanadium for alloy steels, where the chromium contents varies from 16 % to 26 %. Interference from chromium is suspected.

The laboratory decided that ten replicates would be acceptable and that the adjustment values a_2 and a_1 were both equal to zero.

C.3.2 Characteristics of the CRMs selected

Eight CRMs were selected (labelled J, K, L, M, N, O, P and Q).

For vanadium, the certificate information for each CRM is given in Table C.9.

Table C.9 — Certificate information for vanadium

	J	K	L	M	N	O	P	Q
μ	0,011 3	0,012 8	0,036 7	0,042 5	0,093 6	0,120 3	0,172 4	0,195 2
σ_{W0}	0,000 2	0,000 4	0,000 5	0,000 5	0,001 1	0,001 5	0,002 6	0,003 3
σ_L	0,000 4	0,000 7	0,001 2	0,001 8	0,002 4	0,003 5	0,009 4	0,008 9

C.3.3 Results

C.3.3.1 General

The individual data obtained as well as the corresponding mean value ($\overline{X}$) and the estimate of within-laboratory standard deviation (S_D) are given in Table C.10.

Table C.10 — Results for vanadium

	J	K	L	M	N	O	P	Q
Individual data	0,013 2	0,016 8	0,038 5	0,044 9	0,098 5	0,123 7	0,175 0	0,201 0
	0,013 3	0,016 3	0,038 0	0,044 4	0,098 8	0,124 5	0,174 4	0,208 0
	0,013 1	0,016 0	0,037 6	0,045 3	0,097 4	0,125 6	0,173 1	0,204 3
	0,013 4	0,016 7	0,037 8	0,045 1	0,097 8	0,124 3	0,177 2	0,207 8
	0,012 9	0,017 5	0,039 0	0,044 6	0,097 5	0,124 5	0,172 1	0,197 5
	0,013 5	0,016 8	0,038 9	0,044 8	0,097 8	0,123 6	0,171 0	0,209 0
	0,013 3	0,016 9	0,039 2	0,044 1	0,097 5	0,124 4	0,178 1	0,196 5
	0,013 0	0,017 6	0,038 8	0,045 8	0,097 9	0,124 8	0,171 6	0,203 5
	0,013 0	0,016 7	0,039 5	0,046 0	0,097 7	0,122 4	0,172 4	0,207 5
	0,013 3	0,016 1	0,039 3	0,044 3	0,098 5	0,125 5	0,179 3	0,206 5
$\overline{X}$	0,013 2	0,016 7	0,038 7	0,044 9	0,097 9	0,124 3	0,174 4	0,204 2
S_D	0,000 2	0,000 5	0,000 7	0,000 6	0,000 5	0,000 9	0,002 9	0,004 5

C.3.3.2 Evaluation of the precision

The relevant calculations are presented in Table C.11.

Table C.11 — Evaluation of the precision

	J	K	L	M	N	O	P	Q
S_D/σ_{W0}	0,971 8	1,318 7	1,320 6	1,258 0	0,443 7	0,625 4	1,119 7	1,360 9
χ_c^2	0,944 4	1,738 9	1,744 0	1,582 7	0,196 9	0,391 2	1,253 7	1,852 1
$\chi_{9;\,0,95}^2/9$	16,919/9 = 1,880							

For the eight CRMs the condition $\chi_c^2 \le \chi_{table}^2$ is true. Therefore, it can be assumed that there is no evidence that the analytical method is not as precise as required.

C.3.3.3 Assessment of the trueness

The relevant calculations are presented in Table C.12.

Table C.12 — Assessment of the trueness

	J	K	L	M	N	O	P	Q
$\mu - a_2 - 2\sigma_L + 2S_D$	0,010 9	0,012 5	0,035 6	0,040 2	0,089 8	0,115 2	0,163 4	0,186 4
$\overline{X}$	0,013 2	0,016 7	0,038 7	0,044 9	0,097 9	0,124 3	0,174 4	0,204 2
$\mu + a_1 + 2\sigma_L - 2S_D$	0,011 7	0,013 1	0,037 8	0,044 8	0,097 4	0,125 4	0,189 4	0,204 0
ASSESSMENT	**NO**	**NO**	**NO**	**NO**	**NO**	**YES**	**YES**	**NO**

The condition "$\mu - a_2 - 2\sigma_L + 2S_D \le \overline{X} \le \mu + a_1 + 2\sigma_L - 2S_D$" is NOT true in all cases. It is therefore assumed that vanadium determination is interfered by chromium.

C.4 Checking the accuracy of a "Combustion, infrared absorption method" for the determination of carbon in cast irons

C.4.1 Introduction

The laboratory has determined the scope of the method to be 2,0 % to 5,0 % carbon for cast irons.

The laboratory decided that fifteen replicates would be acceptable and that the adjustment values a_2 and a_1 were both equal to 0,03.

C.4.2 Characteristics of the CRMs selected

Four CRMs were selected, (labelled R, S, T and U)

For carbon, the certificate information for each CRM is given in Table C.13.

Table C.13 — Certificate information for carbon

	R	S	T	U
μ	2,059 0	3,029 0	4,002 5	4,813 5
σ_{W0}	0,006 8	0,010 2	0,011 7	0,017 4
σ_L	0,016 0	0,018 0	0,024 5	0,022 1

C.4.3 Results

C.4.3.1 General

The individual data obtained as well as the corresponding mean value ($\overline{X}$) and the estimate of within-laboratory standard deviation (S_D) are given in Table C.14.

Table C.14 — Results for carbon

	R	S	T	U
Individual data	2,006	2,958	3,975	4,746
	1,990	2,976	3,971	4,777
	1,998	2,989	3,941	4,751
	2,015	2,953	3,932	4,772
	1,986	2,987	3,973	4,763
	1,999	2,967	3,956	4,766
	1,993	2,974	3,948	4,740
	2,005	2,976	3,962	4,763
	1,996	2,951	3,951	4,738
	2,012	2,977	3,964	4,767
	1,996	2,982	3,937	4,780
	2,011	2,961	3,942	4,759
	1,999	2,972	3,947	4,749
	1,997	2,954	3,931	4,762
	1,999	2,980	3,950	4,786
$\overline{X}$	2,000	2,970	3,952	4,761
S_D	0,008	0,012	0,014	0,014

C.4.3.2 Evaluation of the precision

The relevant calculations are presented in Table C.15.

Table C.15 — Evaluation of the precision

	R	S	T	U
S_D/σ_{W0}	1,207 4	1,221 1	1,235 2	0,823 6
χ_c^2	1,457 8	1,491 0	1,525 7	0,678 3
$\chi_{14;\,0,95}^2/14$	23,685/14 = 1,692			

For the four CRMs the condition $\chi_c^2 \leq \chi_{table}^2$ is true. Therefore, it can be assumed that there is no evidence that the analytical method is not as precise as required.

C.4.3.3 Assessment of the trueness

The relevant calculations are presented in Table C.16.

Table C.16 — Assessment of the trueness: adjustment value ± 0,03 %

	R	S	T	U
$\mu - a_2 - 2\sigma_L + 2S_D$	2,013	2,988	3,952	4,768
$\overline{X}$	2,000	2,970	3,952	4,761
$\mu + a_1 + 2\sigma_L - 2S_D$	2,105	3,070	4,053	4,859
ASSESSMENT	**NO**	**NO**	**NO**	**NO**

The bias exceeds the prescribed limit, including the adjustment value (± 0,03 %). But, there is no evidence that the bias exceeds the prescribed limit when the adjustment value is increased to 0,05, as shown in Table C.17.

Table C.17 — Assessment of the trueness: adjustment value ± 0,05 %

	R	S	T	U
$\mu - a_2 - 2\sigma_L + 2S_D$	1,993	2,968	3,932	4,748
$\overline{X}$	2,000	2,970	3,952	4,761
$\mu + a_1 + 2\sigma_L - 2S_D$	2,125	3,090	4,073	4,879
ASSESSMENT	**YES**	**YES**	**YES**	**YES**

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