INTERNATIONAL STANDARD

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Iron ores — Certified reference materials — Preparation and certification for use in chemical analysis

Minerais de fer — Matériaux de référence certifiés — Préparation et certification pour l'emploi en analyse chimique

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 11459 was prepared by Technical Committee ISO/TC 102, *Iron ores,* Subcommittee SC 2*, Chemical analysis.*

Annexes A and B form an integral part of this International Standard. Annexes C and D are for information only.

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet central@iso.ch
X.400 c=ch; a=400net; p=iso; o=isocs; s=central

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Introduction

This International Standard is intended for use in conjunction with other International Standards for the chemical analysis of iron ores prepared by ISO/TC 102. It follows the principles described in ISO Guides 30, 31, 33 and 35 (see clause 2 and annex D) on the same subject prepared by ISO/REMCO, modified to take into account the special needs of the iron ore analytical community.

The accuracy (precision and trueness) of International Standard methods for the chemical analysis of iron ore has been assessed under international conditions during the development of this International Standard. This accuracy can be achieved, in practice, only if all conditions stated in the standard document are met. To ensure that these conditions are met, an accuracy control mechanism is included in all recently published International Standards for the chemical analysis of iron ores.

The precision control is achieved by using methods described in ISO 5725-2. The trueness control is achieved by using certified reference material (CRM) iron ores. To work properly, the CRM must be prepared and characterized using high-quality standard methods. This International Standard is designed to give the minimum requirement for producing CRM iron ores of sufficient quality for use in conjunction with International Standards for the chemical analysis of iron ores.

Iron ores — Certified reference materials — Preparation and certification for use in chemical analysis

1 Scope

This International Standard specifies requirements for certified reference material (CRM) iron ores for chemical analysis in terms of

chemical and physical characteristics;

methods of preparation;

methods of characterization and certification.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 4701:—[1)], *Iron ores — Determination of size distribution by sieving.*

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 5725-4:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 4: Basic methods for the determination of the trueness of a standard measurement method.*

ISO 11323:1996, *Iron ores — Vocabulary.*

ISO Guide 30:1992, *Terms and definitions used in connection with reference materials.*

3 Definitions

For the purposes of this International Standard, the definitions given in ISO 11323 and ISO Guide 30, as well as the following, apply:

1) To be published. (Revision of ISO 4701:1985)

3.1 iron ore: Any rock, mineral or aggregate of minerals, natural or processed, from which iron can be produced commercially.

NOTE — The principal ferriferous minerals occurring in iron ores, either singly or severally, are

a) red, brown and specular hematites, martite and maghemite;

b) magnetite;

c) hydrated iron oxides, including goethite, limonite and limnite;

d) iron carbonates, including siderite or chalybite, ankerite and other mixed carbonates;

e) roasted iron pyrites or pyrite cinders;

f) ferrites (e.g. calcium ferrite) occurring sometimes in natural ores, but mainly in fluxed pellets and sinters.

Also included are manganiferous iron ores and concentrates that contain not more than 8 % manganese (dry weight basis after heating to 105 °C).

Excluded are finely ground ferriferous minerals used for pigments, glazes, dense media suspensions and other materials not related to iron-making.

3.2 reference material (RM): Material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.

3.3 certified reference material (CRM): Reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes its traceability to an accurate realization of the unit in which the property values are expressed, and for which each certificate value is accompanied by an uncertainty at a stated level of confidence.

3.4 certified reference material iron ore: A CRM prepared from an iron ore for the purpose of chemical analysis.

3.5 homogeneity: The condition of being of uniform structure or composition with respect to one or more specified properties. A reference material is said to be homogeneous with respect to a specified property if the property value, as determined by tests on samples of specific size, is found to lie within specific uncertainty limits, the samples being taken either from different supply units (bottles, packages, etc.) or from a single unit.

3.6 between-units variation: The variation of the mean characteristic value between units of material.

3.7 stability: The ability of a reference material, when stored under specified conditions, to maintain a stated property value for a specified length of time.

3.8 expiration date: A date, stated by the manufacturer and confirmed by the certifying authority, supplied together with a reference material, indicating the end of the period of validity of use of the reference material for reference purposes when it is stored under specified conditions.

3.9 sample: A representative quantity of material extracted from a batch of reference material.

3.10 test portion: The mass of material extracted from a unit of material for analysis.

3.11 within-unit, between-test-portions variation: The expected value of variation of the characteristic value between test portions taken from the same unit of material.

3.12 certified value (of a given quantity)**:** For a certified reference material, the value that appears in the certificate or other documentation accompanying the material, this value having been certified by a technically valid procedure.

3.13 uncertainty: That part of the expression of the result of a measurement that states the range of values within which the "true" value is estimated to lie within a stated probability.

3.14 accuracy: The closeness of agreement between the "true" value and the measured value.

3.15 best estimate (of the value of a given quantity)**:** An estimate of the value that is optimized by taking into account both metrological and technical judgement and statistical factors.

3.16 interlaboratory test: A series of measurements of one or more quantities performed independently by a number of laboratories on samples of a given material.

3.17 precision: The closeness of agreement between mutually independent test results obtained under prescribed conditions.

3.18 trueness (accuracy of the mean)**:** The closeness of agreement between the average value obtained from a large series of observations and an accepted reference value.

NOTE — The measure of trueness is usually expressed in terms of bias.

3.19 bias: The difference between the expectation of the observed values or test results and an accepted reference value.

3.20 reference method: A thoroughly investigated method, clearly and exactly describing the necessary conditions and procedures for the measurement of one or more property values, that has been shown to have trueness and precision commensurate with its intended use and that can therefore be used to assess the accuracy of other methods for the same measurement, particularly in permitting the characterization of an RM.

3.21 certification: The procedure for establishing, by technically valid operations, the measured values of one or more quantities of a material or substance. The procedure leads to the issuance of a certificate or equivalent documentation.

3.22 reference material certificate: A document certifying one or more property values for a certified reference material, stating that the necessary procedures have been carried out to establish their validity.

3.23 certification report: A document giving detailed information, supplementary to that contained in a certificate, on the methods of measurement used in obtaining the certified value(s) for a given reference material, and a summary of the results obtained (including a description of all factors affecting accuracy), and a description of the way the results were treated statistically.

3.24 certifying body: A technically competent body (organization or firm, public or private) that issues a reference material certificate.

4 Physical requirements

4.1 General

CRM iron ores shall be in the form of homogeneous powders.

To ensure stability, CRM iron ores shall contain a minimum of volatile components and shall not be readily oxidizable. Their mineralogical composition shall be such that their homogeneity is maintained during normal use.

4.2 Homogeneity

CRMs shall be homogeneous with respect to

a) the certified elements;

b) other elements and/or physically characteristics that influence the accuracy of the analytical method(s) used to characterize the certified element content.

The CRM shall have been physically homogenized by means of pulverization and blending. Its homogeneity shall have been tested using analytical method(s) that have precision comparable with those of the anticipated user's methods.

4.3 Particle size

The particle size of a CRM shall be –100 µm for ores having a combined water content of 2,5 % or less and a sulfur content of 0,2 % or less. For other ores, the particle size shall be –160 µm. The particle size distribution shall be determined in accordance with ISO 4701.

5 Preparation

5.1 Pulverization and homogenization

Most reference material iron ores are subjected to a preparation procedure that includes pulverization, homogenization and subdivision into usable units. In this case, the material shall be crushed, ground, sieved and blended in well tested devices. Excessive contamination by abrasion of the crushing and grinding media shall be avoided.

NOTES

1 Because of possible contamination during pulverization, the composition of a powdered reference material may be different from that of the starting material. Therefore, a reference material should not be considered as representative of any type of ore except of itself.

2 It may be necessary or desirable to eliminate, by sieving, any fraction containing constituents that are too hard to grind or could cause future heterogeneity.

5.2 Homogeneity test

5.2.1 General

By nature, iron ore is inhomogeneous. For practical purposes, it is necessary to define the concept of *sufficiently homogeneous* for the intended use. The inference taken from the results of the homogeneity test as to whether the material is sufficiently homogeneous depends on the analytical method used and the test portion size. For the purpose of this International Standard, one will further introduce the concept of *between-units variation and within-unit, between-test-portions* variation.

The material is said to be *sufficiently homogeneous* with respect to a certain characteristic if the homogeneity test results show that the difference between the between-units variation and the within-unit variation is statistically insignificant.

The homogeneity test shall be performed at the following three levels (see annex A):

a) *During blending*: Samples shall be taken from various locations in the blender and analysed.

b) *Control after subdivision into units (bottles)*: Samples shall be taken from randomly selected units and analysed.

c) *Overall control*: The homogeneity of the material shall be confirmed by the results of the interlaboratory test programme.

NOTE — The procedure and results of homogeneity testing should be included in the preparation and characterization report that is made available to users.

5.2.2 Analytical method

The analytical method used for homogeneity testing for a given characteristic shall be at least as precise as the average user's methods for the same characteristic. The test portion size for this test shall be of the same magnitude as that used by the average user's methods. The trueness of the method is not of prime importance for this purpose.

5.2.3 Experimental design

The homogeneity test experiment for level b) of 5.2.1 shall be designed in such a way that an inference can be made from the results as to whether the difference between the between-units variation and the within-unit variation is statistically significant. It is important to randomize the test schedule to avoid any ambiguity between the variation due to the variation in the characteristic and the time drift.

5.2.4 Statistical evaluation of analytical results

The statistical technique used to analyse the test results depends on the experimental design. The analysis of variance (ANOVA) technique (annex B) is one of the common techniques used for this purpose. A significance level $\alpha = 0,05$ is recommended for the test of significance.

5.2.5 Inference

There are three possible outcomes that can be inferred:

a) The difference between the between-units variation and the within-unit variation is not statistically significant. In this case, the material is considered to be homogeneous. The material is homogeneous with respect to the primary characteristics.

b) The difference between the between-units variation and the within-unit variation is statistically significant, but the magnitude of the between-units variance is small from the user's point of view (from a practical consideration). In this case, the material can be considered as sufficiently homogeneous.

c) The difference between the between-units variation and the within-unit variation is statistically significant, and the between-units variance is significant from the user's point of view (from a practical consideration). In this case, the material is considered inhomogeneous and shall not be used as a candidate for preparation as a reference material.

6 Certification

6.1 Characteristics

There are two groups of characteristics of concern:

a) *Primary characteristics*: chemical or physical parameters that are to be certified.

b) *Secondary characteristics*: physical and/or chemical characteristics that are not to be certified, but their presence may affect the uncertainty of the value of the primary characteristics.

6.2 Analytical method

For certification, the primary characteristics should be determined using more than one analytical method if alternative methods are available. At least one of them should be an internationally recognized method or a reference method. If an ISO method exists, it shall be used.

6.3 Interlaboratory test programme

6.3.1 General concept and practice

The concept of the certification of an RM by an interlaboratory test programme is based on at least two statistical assumptions:

a) There exists a population of laboratories that are equally capable of determining the characteristics of the RM to provide results having acceptable accuracy. This assumption implies that the differences between individual results, both within laboratory and between laboratories, are statistical in nature regardless of the causes.

b) There exists a consensus value, i.e. the distribution of the results follows a uni-modal distribution.

It is recognized that, in practice, the size of the laboratory population that is available to an interlaboratory analysis programme is limited. In most cases, therefore, a random-design model cannot be fully implemented.

6.3.2 Organization of interlaboratory programme

The interlaboratory programme shall have a well defined objective, be effectively designed and be efficiently organized with clear, concise guidelines with which participating laboratories can readily comply. The guidelines shall include the time objective, the number of units, the number of replicate determinations per unit and the method of reporting data, such as the description of the analytical method used and the number of digits to which the analytical results are to be reported.

6.3.3 Experimental design

6.3.3.1 Choice of laboratories

The participating laboratories shall be chosen from the population of laboratories that are competent in iron ore analysis.

6.3.3.2 Number of laboratories p

The minimum number of usable laboratory results p shall be 10. Each laboratory shall be requested to analyse the sample by a method of its own choice (the best method available that conforms with 6.2).

6.3.3.3 Number of replicate determinations per laboratory n_i

The number of replicate determinations required per participating laboratory depends on the system used. The choice of systems is as follows:

a) *One-unit system*: Each laboratory is given *one* randomly selected unit to be analysed. In this case, a minimum of three independent determinations ($n_{i,\ \mathrm{min}} = 3$) is required. This system is used if it is certain that the material is homogeneous.

To confirm homogeneity among units, at least one laboratory shall analyse a series of randomly selected units.

b) *Two-unit system*: Each laboratory is given *two* randomly selected units of sample to be analysed. In this case, the minimum required is duplicate determinations per unit of sample (i.e. $n_{i,\ \mathrm{min}} = 4$).

In the case of a one-unit system, the number of replicate determinations to be performed by each laboratory need only be approximately equal. In the case of a two-unit system, the number of replicate determinations per unit to be performed by each laboratory shall be identical.

6.3.3.4 Time objective

It is important that the whole certification programme be completed within a reasonably short time (i.e. four to six months).

6.3.4 Evaluation of the results of the interlaboratory certification programme

6.3.4.1 Scrutiny of the results

The analytical results shall be scrutinized for

a) possible physical errors such as test portion size, transcription errors;

b) the use of an inappropriate analytical method.

6.3.4.2 Graphical presentation

It is recommended that the analytical results be listed in graphical form. Figure 1 is an example of a graphical presentation. Information such as the frequency distribution, homogeneity and outliers can sometimes be observed from the graphical presentation of the analytical results.

6.3.4.3 Determination of the certified value and its uncertainty

The certified value shall be determined using all analytical results collected from the interlaboratory test programme excepting those that are considered as chemical or physical outliers. The analytical results shall follow a uni-modal frequency distribution. The certified value shall be derived from the overall mean of all the results if the numbers of laboratory results are approximately equal, or from the mean of the laboratory means if the numbers of laboratory results are not equal. Its precision shall be estimated by analysis of variance (ANOVA) methods. The trueness and precision shall be calculated in accordance with ISO 5725-4 and ISO 5725-2, respectively, for the interlaboratory certification test programme. These values shall be included on the certificate. Details of the calculation are given in annex A.

6.3.4.4 Criteria for acceptance

The mean is accepted as the certified value for a particular element content if it satisfies the following criteria:

a) that all analytical results used for certification were obtained by methods which are chemically justified for the purpose;

b) that the average within-laboratory precision of all these methods is no greater than that of the available ISO method(s);

c) that the ratio of the confidence interval of the certified value to the average of the within-laboratory standard deviations of the methods is not greater than 5.

7 Content of certificate

The certificate shall contain the following:

a) the name and address of the certifying organization;

b) the title of the document;

c) the status of the certificate;

d) the name of the material;

e) the sample number and/or batch number;

f) the date of certification;

g) the source of the CRM;

h) the supplier of the CRM;

i) a complete description of the CRM;

j) a statement of intended use;

k) stability, transportation and storage instructions;

l) special instructions for correct use;

m) the method of preparation;

n) a statement of homogeneity;

o) the certified values and their uncertainty, the latter expressed in terms of the within-laboratory standard deviation s_{wc} and the between-laboratories standard deviation s_{Lc};

p) the values of any secondary characteristics, given for information but not certified;

q) any special values obtained by individual laboratories or methods;

r) the meaning of statistical uncertainty;

s) the measurement techniques used for the certification;

t) a legal notice;

u) the date of the last review;

v) reference documents (including a companion report if any).

NOTE — It is strongly recommended that a more detailed report describing the method of preparation and certification of the CRM be made available.

8 Periodic review of the certificate value

It is recommended that CRM producers review periodically, at least every five years (see note), the certified values, incorporating new information pertaining to the particular CRM.

NOTE — The review may be carried out at an interval of less than five years if a problem is observed with the reference material.

The certificate shall be updated if necessary and the producer shall inform the users of any change resulting from the periodic review. This review is mandatory only if the CRM is relevant to currently traded iron ores. Reviews shall be undertaken also for the recertification of elemental components as improvements and/or modifications in, or complete replacement of, approved ISO methods arise.

9 Customer record

The producer of the CRM shall maintain a good record of the names and addresses of the users (customers). The producer shall notify the customers of any change regarding the CRM, i.e. changes in the certified values due to the availability of new information.

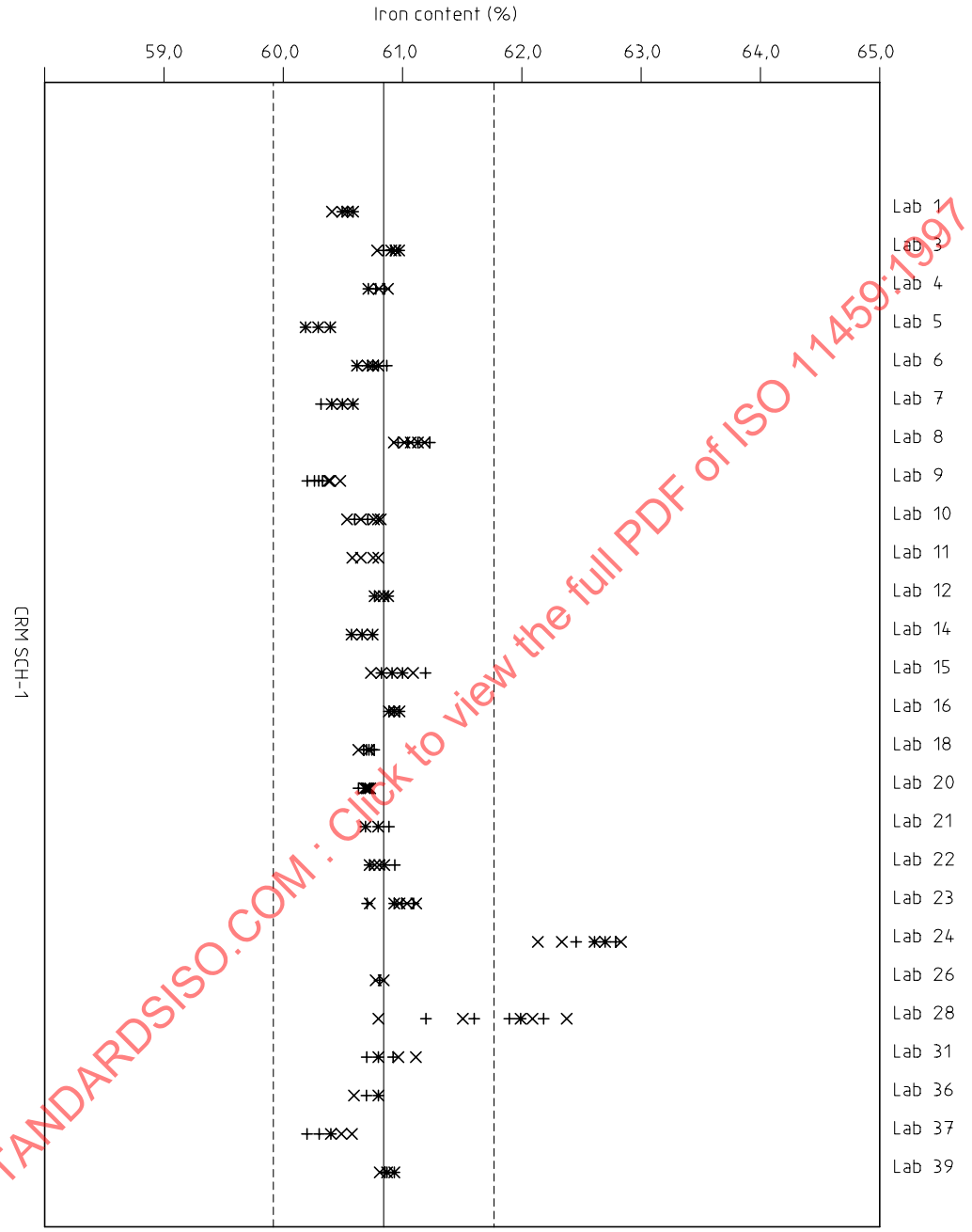

Figure 1 — Example of graphical presentation of results of interlaboratory analysis

Annex A
(normative)

Confirmation of the homogeneity of a CRM candidate by results of an interlaboratory analysis programme

A.1 General

The results of an interlaboratory analysis programme can be used to confirm the homogeneity of a CRM candidate.

A.2 One-unit system

Between-laboratories variation, as expressed in terms of σ_{Lc}^2 in annex B, includes the variation due to the analytical method(s) used for characterization and the between-units variation of the material. The magnitude of this variation determines the acceptability of the CRM candidate for certification. If the precision of the analytical method(s) is known, the existence and the magnitude of the between-units variation can be estimated.

A.3 Two-unit system

The results of an interlaboratory programme using a two-unit system produce more information on the homogeneity of the CRM candidate, as follows:

a) *Graphical observation*: Inspection of figure 1 may show the homogeneity of the material. Significant separation between the analytical results of different units indicates inhomogeneity.

b) *Comparison of the unit means*: If the number of replicate determinations per unit of sample is large ($n_{ik} > 3$), a series of *t*-tests for comparison of the unit means reported by the same laboratory can be performed to confirm the graphical observation.

c) *Two-way analysis of variance*: If a significant number of laboratories uses the same or similar analytical methods, a "two-way-nested ANOVA" method shall be used to determine the significance of the between-units variation of the candidate CRM. Detailed computation of this ANOVA is described in ISO/TC 102/TCR 5.

Annex B
(normative)

Detailed computation of analysis of variance

B.1 One-way-nested design

This model is used when it is accepted that the material is homogeneous, i.e. that the between-units variation is insignificant. In this case, the difference between the results reported by different laboratories is caused by the difference in the method used and by other laboratory-associated factors such as the environment, analyst and calibration.

The model is

$$x_{ij} = \mu + \alpha_i + e_{ij}$$

where

x_{ij} is the jth result reported by laboratory i;

μ is the consensus value which is estimated by the overall mean of the results;

α_i is the bias of laboratory i;

e_{ij} is the statistical error associated with laboratory i and result j.

The assumption is that both α_i and e_{ij} are normally distributed with means of 0 and variances of σ^2_{Lc} and σ^2_{wc} respectively. Detailed computation of this ANOVA is described in ISO/TC 102/TCR 5[8] (see annex D).

B.2 Computation of the consensus value and its uncertainty

$$\bar{x}_i = \left(\sum_{j=1}^{n_i} x_{ij} \right) / n_i$$

$$\bar{x} = \left(\sum_{i=1}^{p} \bar{x}_i \right) / p$$

where

n_i is the number of results reported by laboratory i;

p is the number of laboratories.

The variance of the consensus value $\bar{x}$ is given by

$$V(\bar{x}) = \left[\sum_{i=1}^{p} (\bar{x}_i - \bar{x})^2\right] / (p-1)$$

with (p-1) degrees of freedom.

The confidence interval for the consensus value is the interval from A to B

where

$$A = \bar{x} - t_{1-\alpha/2,\,(p-1)}\left[V(\bar{x})\right]^{1/2}$$

$$B = \bar{x} + t_{1-\alpha/2,\,(p-1)}\left[V(\bar{x})\right]^{1/2}$$

$t_{1-\alpha/2,\,(p-1)}$ being the $1-\alpha/2$-fractile of the t-distribution with $(p-1)$ degrees of freedom.

Once the certification programme is complete, the consensus value is then accepted as the certified value A_c.