GUIDE 31

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Contents of certificates of reference materials

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

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GUIDE 31-1981 (E)

Contents of certificates of reference materials

0 Introduction

This document is an outcome of the collaboration of ISO Committee on reference materials (REMCO) with the following international organizations : EEC, IAEA, OIML, IUPAC and WHO. The first draft was prepared by Mr. T. W. Steele of the "National Institute for Metallurgy (SABS)".

Although the amount of information that is given on certificates of reference materials varies considerably, this variation is only partly accounted for by the varying nature of the material. Thus, certificates of even basically the same type of material issued by different producers vary from a bare statement of the value of the certified property to a lengthy document containing very detailed information, some of it not always relevant to the reference sample. Some producers do not issue certificates at all but expect the user to search for the information in publications which may not be readily available.

This diversity in the character of certificates has come about because the essential function of a certificate has not always been appreciated. The true nature of a certificate can best be appreciated if the certificate is compared with two other sources of information on a reference material. These are the label and the report : the former is normally affixed to the sample container, and the latter accompanies the certificate or can be obtained on request.

Usually, because the size of the label is determined by the size of the container to which it is to be affixed, the label can contain only the briefest of information about the reference material and, normally, simply identifies the reference material. The report on the reference material usually contains all the relevant information including the details of the certification procedure. However, because it is so detailed, there is clearly a need for a second document that would condense all the information about the sample. This document is the certificate which can be described as the synopsis of the report. A certificate that is expanded in an attempt to make it serve also as a report defeats its purpose, and is no longer the concise and readily referenced document that it should be.

Traditionally, the certificate has consisted of one or two pages as though the need for a brief synoptic document has always been intuitively felt to be appropriate. Apart from the desire for brevity, there was little need for a detailed certificate because the certified information was taken on trust. Except until comparatively recently, certified reference materials were produced by only a few specialist organizations whose reputations were such that their names were a sufficient guarantee of the integrity of the reference material. With the increase in the number of producers this assumption is no longer acceptable because no matter how high the reputation of the producers in their scientific and technological fields, it does not follow that this reputation is necessarily transferable to the fledgling reference material. Parallel with the increase in the number of new producers there has been a demand for a reference material of higher quality, a consequence both of the increased precision of measuring equipment and the need for more accurate data in the scientific and technological disciplines. In illustration of this trend, producers freely admit that their old reference materials may not meet the more stringent requirements of today. Whereas formerly it did not seem to be of much importance to know the bounds of uncertainty of a certified value other than in some intuitive fashion, users are now becoming increasingly more critical of certificates that do not give this information. The user needs not only this information but also the details of the whole certification procedure. In other words, not only must the certified value be accurate but it must now be seen to be accurate. In recognition of this need, the latest certificates of producers of long-established reputation are becoming more detailed and sometimes take on the character of a report. On the other hand, as has been mentioned, many of the younger producers issue detailed reports without certificates. The certificate is thus in danger of losing its useful synoptic character, or in some areas of becoming extinct. This eclipse of the certificate *per se* is unfortunate, and appears to arise from the fact that the distinction between a certificate and a report on the reference material has not been clearly recognized.

In summary, a certificate should communicate information about a reference material from the producer to the user; in essence, this information is a statement of the certified property values, their meaning, and their confidence limits.[1] The remainder of the information is peripheral to this central statement and has two purposes : to describe the general nature and use of the material, and to assure the user of its integrity. In a well-prepared certificate, the information should be presented in a form that enables the user to draw his own conclusions about the integrity of the certified material.

This Guide is intended to help producers to prepare clear and concise certificates, which, while maintaining the essential character of a certificate, should help to provide, in summary form, all the information needed by the user of the reference material.

1) The term "uncertainty" in place of "confidence limits" is sometimes preferred (see ISO Guide 30).

1 Scope and field of application

A series of headings is given in clause 2 to indicate the information that should be provided on a certificate. An explanation is given under each heading, together with examples where more clarification seemed to be necessary. In the compilation of these headings, the aim was to cover the required information on as wide a range of reference materials as possible, taking into account such diverse examples as a triple-point cell, a microscope magnification standard, a powdered rock, and a biological material. Some of the headings may not be needed for a particular material but these are likely to be the exception rather than the rule. The headings are given in what seems to be a logical order for the presentation of the information, which in summary is as follows : the general particulars of the certifying organization and the reference material [name, sample, number, date of certificate, etc. (see 2.1 to 2.10)]; a description of the material and its intended use (see 2.11 to 2.16); the certified values, their confidence limits, and an explanation of these values and the techniques used for their measurement (see 2.17 to 2.21); the references and the names of participating analysts and certifying officers (see 2.22 to 2.25).

It should be emphasized that this Guide is concerned with the informational contents of the certificate and not its style or format. Thus, the order of headings and the wording of the headings may be changed to suit the reference material or the preferences of the producer.

2 Certificate headings

2.1 Name and address of the certifying organization

This name (usually given in prominent type at the head of the certificate) should be that of the body or organization that accepts responsibility for the information on the certificate. Cooperating laboratories or an organization that may only have prepared the sample are preferably given elsewhere (see 2.21).

2.2 Title of the document

There should be a distinct title. Common titles are

Certified reference material certificate of analysis

Certificate of a reference material

2.3 Status of the certificate

Some certificates are of a provisional nature, and this qualification when appropriate, should be clearly stated.

2.4 Name of material

As far as possible, the name should distinguish the type of reference material. Thus, "triple-point cell, diphenyl ether" is preferable to just "triple-point cell". The name of the rock or ore followed by its locality or a compositional characteristic gives more individuality to geological materials; for example, "Syenite (Phalaborwa)" or "Nepheline syenite". For metallurgical samples, it is appropriate to give the concentration of an important element, for example "Carbon steel 0,14 %".

2.5 Sample number (and batch number)

Each reference material should be numbered, the number preferably being accompanied by the initials of the certifying organization, for example "BCS No. 260". The practice adopted by the National Bureau of Standards of following the number with a letter (*a* to *z*) to identify a renewal of the original material is recommendable.

2.6 Date of certification

In addition to the original date of certification, the dates of all revisions should be given.

2.7 Availability of other forms or sizes of the reference material

This information need be given only in relation to the material named on the certificate. Thus, there can be one or more packaged units supplied or, as frequently happens with metallurgical samples, a metal or alloy may be available in the form of chips and discs.

2.8 Source of the reference material

A knowledge of the origin or source of the material constituing the reference material could be useful background information for the user. The geographical location of a rock sample, for example, is of special interest to geologists and geochemists. On the other hand, the supplier may not wish to have the composition of his material identified since it might reveal confidential information on his commercial material.

2.9 Supplier of the reference material

The name and address of the organization from whom the reference material can be obtained should be given if the certifying organization is not the supplier.

2.10 Preparer of the material

The preparation of the material might be undertaken by an organization other than that which undertook the testing and certification. The comminution of ores, the melting and casting of metals, the manufacture of chemicals, and the fabrication of equipment that is an integral part of the reference material, are all important parts of the production of a reference material and can have a vital bearing on the homogeneity and stability of the material. The organization that undertakes this work should therefore be given this recognition.

2.11 Description of the reference material

The general description of the material should, in effect, amount to a detailed explanation of the name of the material, for example "The triple-point cell contains approximately 150 g of highly purified phenoxybenzene and has been evacuated of air before sealing." For a biological material, part of the description could be "The material has been preserved with benzoic acid". For compositional material, there could be a description of the main constituents that do not appear in the table of certified values, and for geological material, the mineral composition could be given.

A description of the physical character of the material is also appropriate under this heading.

Examples :

— "This reference material is in the form of discs 31 mm in diameter and 14 mm thick"

— "The reference material consists of three filters in special holders"

— "The material has been ground to pass a 200-mesh sieve"

— "The sample of gas is supplied in a steel cylinder at 12,4 MN/m^2 pressure"

Toxic or hazardous (for example radioactive) ingredients in the material should be mentioned and, if circumstances warrant it, a warning should be given in bold type.

2.12 Intended use

The purpose for which the reference material was issued should, as far as possible, be clearly stated so that it is not misused. For example, a reference material of a mineral may be suitable for methods of analysis that require a relatively large mass of subsample but would be totally unsatisfactory as a reference material for the electron-microprobe technique.

The following are examples of entries appropriate to this heading :

— "The reference material is intended for the calibration of the magnification scale of a scanning electron microscope to an accuracy of 5 % within the range of 1 000 to 200 000 magnifications"

— "Intended for the realization of a fixed temperature point on the practical temperature scale and, therefore, for the calibration of temperature measuring equipment"

— "A reference material intended for the following :

a) for calibration of instruments for determining the concentration of precious metals in ore samples;

b) as an arbitration sample for commercial transactions;

c) for the verification of analytical methods for precious metals;

d) for the preparation of secondary reference materials of similar composition.''

2.13 Stability, transportation, and storage instructions

As the reference material (and, therefore, the certified values) can be affected by numerous factors such as temperature, light, and exposure to the atmosphere, a description should be given of the conditions of transportation, handling, and storage that are most favourable to the maximum lifespan of the sample.

Wherever possible, the period of validity of the reference material should be stated. When the stability is suspect but known exactly, a statement such as the following would at least introduce a cautionary note :

''It is possible that ageing of the glass may cause the filters to change transmittance by about 1 % over a period of approximately 1 year. Tests have shown that, in a normal laboratory atmosphere (absence of direct sunlight and temperatures of 10 to 30 °C), the sample is stable for 1 year. The purchaser will be notified if deterioration occurs beyond that period.''

2.14 Instructions for the correct use of the reference material

These instructions are often essential in that the certified values are normally applicable only when the user adheres to the instructions that the certifying analysts were asked to follow. The following are examples of such instructions :

- ''Dry the sample at 105 °C for 2 h before use''
- ''Remove surface oxidation on the specimen by etching for 45 to 60 s in a solution of nitric acid (relative density 1,4) at 20 °C. Rinse in distilled water and dry in hot air at about 60 °C''
- ''The specimens should be handled only by the edges with plastic gloves''
- ''Should the surface become contaminated, the sample should be returned to the producer for cleaning and recalibration''

Blending and subsampling instructions have their place under this heading, and also any warnings, for example ''trace-element values might be affected by contamination products of the grinding and blending equipment.''

For some reference materials, the instructions are so detailed that they are preferably issued in an annex to the certificate. The entry under this heading should refer the reader to an annex of the certificate.

The method of measurement is sometimes an inseparable part of the reference material. This applies particularly to empirical measurements of ''technological'' properties such as hardness values, and colour fastness. These detailed methods should also be stated in an annex to the certificate.

2.15 Method of preparation of the reference material

This information is applicable to most types of reference material : it enables the user of the reference material to form a judgement on the amount of planning and care that has been exercised by the producer, and thus to judge the quality of the reference material, and, to a more limited extent, its possible state of homogeneity and stability. Although the proper place for this information is in the report, a summary is needed for the certificate.

An example of an entry under this heading is the following :

- ''The leaves for this sample were hand-picked and air-dried. The dried leaves were ground in a comminuting machine to pass a 40 mesh sieve. The ground material was dried at 85 °C, mixed in a feed blender, packed in polyethylene fibre drums, and sterilized *in situ* with 49 kGy* radiation from a cobalt isotope.''

2.16 State of homogeneity

Despite the fact that a high degree of homogeneity is probably the most important criterion of many reference materials, many certificates do not mention the state of homogeneity of the sample. Certainly, a brief description should be given of the tests that were conducted to test the degree of homogeneity and, since homogeneity is relative to the given mass of the sample, the mass of subsample at which the homogeneity was tested should be given.

* 49 kGy = 4,9 Mrad = 49 kJ/kg

Mathematical expressions exist for the degree of homogeneity of powdered material such as ores and rocks, the best known being the sample constant of Ingamells and Switzer[1], defined by

$$K_s = s^2 m$$

where

s is the relative standard deviation in per cent for one component of the sample (i.e., the subsampling uncertainty);

m is the subsample mass.

The sampling constant K_s, which can be determined experimentally, is the mass of subsample necessary to ensure a relative subsampling error of 1 % (68 % confidence level) in a single determination.

2.17 Certified property values and their confidence limits

The information under this heading should be given in tabular form with the confidence or uncertainty limits to the right of the property value. Notes to the headings "Certified value" and "Confidence limits" should direct the reader to separate sections in the certificate (see 2.20) that provide information on the statistical treatment of the measurement values used for the calculation of the certified value and its confidence limits.

The way the information on the method of measurement is given depends on the circumstances. If only one property is certified, the relevant heading number (see 2.21) can be placed next to the value to direct the reader to the section that gives a short description of the method. When there are several certified values for different properties of the sample, and therefore several methods, letters placed next to the values can be used to refer the reader to the section listing methods of measurement. The table should, of course, be accompanied by a footnote stating that a key is given under the relevant heading (see 2.21).

A similar system (preferably using numbers instead of letters) can be used if the producer wishes to identify the certified value with the participating analysts or laboratories. (See 2.22 for the key to analysts and laboratories).

Footnotes to the table could give information on the state of the material at the time of measurement (for example "values on sample dried to constant mass at 105 °C)". Other relevant information could include the time and date if the value is the result of a radioactivity measurement.

An example of a tabular presentation of the certified value is given below :

Constituent and formula for reporting	Certified value[1] %	95 % confidence limits		Method of analysis (letter)	Analysts (numbers)[2]
		High	Low		
Aluminium, Al	0,73	0,77	0,69	B	1, 2, 5
				A	2, 3
Chromium, Cr	0,94	0,96	0,92	C	2, 4, 9
				D	5, 6, 7
				E	2, 9, 10
Vanadium, V	0,12	0,14	0,10	F	3, 6, 7

1) The meaning of the certified value and the confidence limits is given in Section ... (See 2.20 of this Guide)

2) The keys to the methods of analysis and the analysts are given in Sections ... and ... respectively (See 2.21 and 2.22 of this Guide).

In exceptional instances, the certified information is given as a diagram and not in numerical terms. An example is the certificate for folic acid issued by the World Health Organization, Center for Chemical International Collaborating Reference Substances, in which a chart-recording of the infrared absorption is presented as the certified information. Such a chart can legitimately take the place of the table.

A distinction should be made between certified values and values that cannot be given with a high degree of confidence. The latter are best given under a different heading (see 2.18). Although there is no generally accepted definition, a certified value for the purposes of this Guide is a value based on the results of two or more methods of analysis that agree within acceptable limits or, if only one method of measurement can be used, on measurements by more than one independent investigator.

2.18 Uncertified values

Producers might obtain values for constituents or properties of a reference material that do not qualify as certified values. This information about the material may nevertheless be of value to the user, and should therefore be given on the certificate, preferably in a

second table with an appropriate heading such as "Approximate value", or, if the value is of a still lower degree of certainty, "Magnitudes", so as not to confuse these values with the certified values.

2.19 Values obtained by individual laboratories or methods

Certified values are often obtained as a mean (or some other estimator of central tendency) of the results obtained by more than one method of measurement by the same analyst, or by more than one participating laboratory. The value of a certificate will be enhanced if the separate results used in the estimation of the certified value are given (preferably in a separate table, together with an identification of the technique used); the user could then place subjective interpretations on the certified value depending on his knowledge of the measurement techniques.

2.20 Estimator and confidence limits of the certified value

The meaning and nature of the certified value should be given, i.e., the statistical estimator should be named. For example, the estimator could be the unweighted mean, the median, or the mode of several measurements. Where the estimate is a more complex one, the mathematical expression, which is unambiguous, should be given.

When subjective considerations have entered into the assignment of the certified value (for example, where several laboratories have used different methods of analysis and the producer has given greater weight to those techniques that he has felt to be more accurate) explanation should be given of the nature of this reasoning. However, to retain the synoptic character of the certificate, there should be a reference to the report on the reference material, where there should be a full description of the mathematical treatment of the measurement values.

A description is also needed of how the confidence limits (see 2.17) were calculated in order to make their meaning clear. The most precise way of giving this information is in the form of mathematical formulae that are available for the confidence limits for most of the more commonly used estimators of central tendency, such as the mean or median.

It should be noted that the common practice in which a plus and minus value is placed next to the certified value without explanation can be interpreted in at least four different ways :

a) it could be the Student's t-value multiplied by the standard deviation of a single determination;

b) the Student's t-value multiplied by the standard deviation of the mean;

c) the range of all the analytical values;

d) a subjective range of the certified value.

Also ambiguous are statements of the type "the total error does not exceed ± 8 %".

In some cases it may not be possible, or even appropriate, to give rigorously calculated confidence limits. For example, most common estimators of central tendency are applicable only if the distribution of the measurement values approximates a Gaussian distribution. This frequently does not apply to trace constituents in a reference material. In such instances, the producer is entitled to place subjective confidence limits to the certified value, based on his knowledge of the measurement techniques used for the certification. The producer should clearly state when subjective decisions have been made and, if possible, provide supplementary information such as a measure of the spread of the values. Such supplementary information should allow the user to judge the uncertainty of the certified value. (For further discussion on appropriate statement of confidence of the certified value, see bibliography[2] [3] [4].)

The following is an example of an appropriate entry under this heading :

"The certified value is the grand mean of the 40 replicate values of the 10 participating laboratories computed according to the formula

$$\bar{x} = \frac{\sum_{i=1}^{i=k} \sum_{j=1}^{ni} x_{ij}}{\sum_{i=1}^{i=k} n_i}$$

where

x_{ij} is the j^{th} value in set i;

n_i is the number of values in set i;

k is the number of sets;

$\bar{x}$ is the grand mean.

The confidence limits were obtained by calculation of the variance of the grand mean and reference to the Student's-t distribution :

$$\sigma^2 = \frac{\sum_{i=1}^{k} n_i^2 \sigma_L^2}{\left(\sum_{i=1}^{k} n_i\right)^2} + \frac{\sigma_w^2}{\sum_{i=1}^{k} n_i}$$

where

σ^2 is the variance of the grand mean;

σ_L^2 is the between-set variance;

σ_w^2 is the within-set variance.

The last two variances are estimated from the between-set and within-set mean sequences respectively.

Confidence limits $= \bar{x} \pm t_{0,05}\sqrt{\sigma^2}$

where

σ^2 is the variance of the grand mean;

$t_{0,05}$ is the percentile of the Student's-t distribution for $k-1$ degrees of freedom.

In the calculation of the confidence limits, the assumption was made that the distributions of the values are normal.

[See the report under Reference (see 2.24 of this Guide) for a description of the mathematical model on which these formulae are based.]"

2.21 Measurement techniques used for the certification

Details of the measuring techniques or analytical methods are given appropriately in the report on the reference material, but, in keeping with its synoptic character, the certificate should contain a very short description of the method. When appropriate, the mass of subsample taken for the analysis should be given in the description. When there are many property values for the same material, it may be sufficient to give a list of the techniques with a reference to the report.

2.22 Names of analysts, investigators, and participating laboratories

When laboratories other than the producer's laboratory have participated in the certification programme, it is recommended that the names of these laboratories should be given on the certificate. This practice, apart from giving credit to the participant, allows a subjective interpretation to be made of the quality of the reference material. When the values obtained by the participating laboratories are given (see 2.19), it should be left to the discretion of the producer to identify the analyst with the values in the table.

2.23 Legal notice

Legal restrictions in connection with the procurement, transportation, storage, and handling of the material should be given under this heading. An indemnity clause, if needed, can also be included.

2.24 Reference

The reference given here should be to the report on the reference material, which should include a full account of the procedures used for the preparation and certification of the reference material. A distinction should be made between this report and the references that provide supplementary information for educational purposes. The latter are preferably given in an annex to the certificate.