Guidelines for the Selection and Use of Certified Reference Materials

ILAC-G9:1996

ILAC-G9:1996

Guidelines for the Selection and Use of Certified Reference Materials

PREAMBLE

The final objective against which the aptitude for use of a Certified Reference Material (CRM) is evaluated is its contribution to the uncertainty of the analyses, made by means of the calibration performed with the CRM.

The metrological quality of the analysis is its uncertainty. Other parameters may also be important (cost, speed, practicality), but these must be considered as subordinate to the assurance that the criterion of accuracy meets the level required for use.

This paper exclusively addresses the case in which CRMs are used for calibration. The paper discusses criteria with respect to chemical analyses by general methods, but the concepts can be applied by the reader to other areas of material testing.

Demonstrating the quality of chemical analyses often implies demonstrating the quality of the CRM used for calibration. This point highlights the importance of accreditation of CRM producers.

The reader concerned with this aspect of the problem may refer to Guide ISO-REMCO 34 for guidance and to relevant accreditation bodies for implementation rules.

PURPOSE

These guidelines aim at establishing the framework by which laboratories seeking accreditation, and technical assessors, will be able to propose and evaluate the CRMs relevant to their specific needs.

AUTHORSHIP

These guidelines were prepared by a Working Group of ILAC Committee 3. The Convenor was Dr A Marschal of France.

The guidelines were endorsed for publication by ILAC Resolution No. 17/96.

1. CALIBRATION OF CHEMICAL ANALYSES

The definition of calibration according to VIM (6.13) is *"The set of operations which establish, under specified conditions, the relationship between values indicated by a measuring instrument or measuring system (..) and the corresponding known values of a measurand."*.

For the calibration of an analytical method, the *value indicated by a measuring instrument* is, for example, the optical density for atomic or molecular absorption, the intensity of the current delivered by the flame or plasma emission spectrophotometer, the number of counts of radiation emitted in X-ray fluorescence or activation analysis, or the integral of a peak in arbitrary units specific to the apparatus in gas or liquid chromatography.

Since this signal cannot be related directly by calculation to the concentration of the entity assayed, the correspondence factor is determined by relating the analytical signal given by one (or more) reference materials to its certified value. *The uncertainty on this certified value is selection criterion No. 1.*

Another important aspect of calibration is that it is established *in specified conditions*. This means that if the instrument is used in conditions other than those prevailing at the time of calibration, the calibration values are no longer strictly applicable.

It is obvious to the chemist that a calibration curve plotted in a given instrumental configuration (e.g. length of absorption path, flow-rate or volume of analyte injected) is inapplicable if these parameters are changed. The chemist is also aware of the fact that small fluctuations in these parameters, due to the instability of the instrument or of the environment, will give rise to small fluctuations in the calibration factor, which is reflected by dispersion of the analytical results.

One of the underestimated *specified conditions* is that of the matrix in which the element (or molecule) to be determined is included. This matrix affects the analytical signal by relatively complex mechanisms (which are described in manuals). The *'matrix' specified condition* is in fact the matrix making up the reference material used for calibration. Since it is never strictly identical to those of the samples analyzed, this causes a variation in the calibration factor which then generates a bias in the analytical results.

The bias is slight if the similarity between the sample and the reference material is good, if the "robustness" of the detector with respect to matrix differences is good, or if the samples are appropriately treated before analysis. In these cases, the bias is an acceptable supplementary uncertainty component. If the bias is high and the matching between the reference material, the samples and the method is inappropriate, it becomes a systematic error which is no longer acceptable. *A technically-adapted answer to this problem is selection criterion No. 2.*

These two points lead to the conclusion that the selection of a reference material implies providing a satisfactory answer to these two criteria by granting them similar attention. The COMAR data bank helps to account for these criteria together.

Other uncertainty components must be taken into account in estimating the total analytical uncertainty (ie. instrument, protocol, environment), but these are not directly linked to the CRM related factors.

2. CRM SELECTION

A reference material is selected by comparing the contribution of the reference material to the total analytical uncertainty and by evaluating this as satisfactory, acceptable or incompatible. This operation implies that a total analytical uncertainty is set as a target. This target can obviously be reviewed if necessary. As a first approximation, the ratio between the total uncertainty target and the reference material contribution can be considered as leading to a classification as follows:

$I_T / I_r \geq 10$:	Satisfactory
$10 > I_T / I_r > 4$:	Acceptable
$4 > I_T / I_r > 2$:	Acceptable if no other solution exists; upward revision of I_T undoubtedly necessary
$I_T / I_r \leq 2$:	Unsatisfactory situation; implies reviewing the total uncertainty, the method applied, and the choice of reference material.

I_T = *total uncertainty target*
I_r = *uncertainties deriving from the reference material, accuracy and appropriateness*

The uncertainty specific to the reference material *(selection criterion No. 1)* is evaluated by considering the following points:

a)	An uncertainty is indicated by the producer	(+)
b)	This uncertainty is documented in the certificate, the certification report (+)	
c)	The producer is known for the quality of his CRM	(+)
d)	The producer (or the reference material) is accredited by a competent accreditation system (+)	
e)	No uncertainty is explicitly indicated by the producer, but the user can estimate it by considering the information supplied by the producer, such as the methods employed, interlaboratory reproducibility, etc. *(NOTE: In this type of situation, the user can encourage the producer to supply an explicit uncertainty estimate.)*	(?)
f)	It is impossible to indicate a producer uncertainty *(NOTE: In this type of situation, the user will have to evaluate the uncertainty with his own resources. This task may be difficult, even impossible.)*	0

The uncertainty of appropriateness *(selection criterion for No. 2)* is harder to estimate. It cannot be determined by the reference material producer, since he lacks information about the user's analytical methods, and on the variety of samples analyzed in the actual life of the laboratory.
The following points could be considered:

a) Is the analytical method sensitive to differences in matrix between the CRM and the samples? This applies to the factors of basic composition, specific elements or compounds, viscosity or surface tension of solutions, particle size distribution of powders, etc. This sensitivity can be analyzed experimentally.
b) Would another analytical protocol narrowing these differences yield the same value?
c) Do the laboratory results obtained with the method considered display a systematic bias with respect to other CRM? to values obtained by standard methods? to interlaboratory round robin?
d) Can the use of a set of CRM instead of a single CRM help to "frame" the variety of samples in terms of "matrices" as well as of "certified values" ?

The user can take account of the potential effects identified and treat them as uncertainty components.

3. USE OF CRM

CRMs should be used according to the state of the art and good practice of the different analytical methods employed. They are not dealt with here. The CRM is not intended to substitute for the calibration of instruments (other than the analyzer) such as balances, pipettes or thermometers, which must be calibrated directly.

A number of guidelines and general rules specific to the use of CRM can be enumerated:

a) The conditions of use of CRM should guarantee that the requisite conditions described under "CRM selection" are maintained throughout use.

b) As to the accuracy of the certified value, it is important to ensure that:
   - the CRM does not deteriorate by ageing (oxidation, biodegradation, sedimentation, etc.)
   - it does not deteriorate through use (pollution, evaporation, dilution).

Once a CRM has lapsed, or is dubious, it is normally not recalibrated but replaced by a new one.

It can be compared regularly with an internal reference material or even with a "benchmark" material to check its stability, if the risks of instability are significant.

The CRM is the basis of accuracy; it is unwise to alter its value to compensate for an instrumental, procedural or other error.

To make certain that a CRM is appropriate, it is important to ensure that:

- no sample subjected to analysis deviates from the prerequisites of matrix similarity,
- the instrumentation and analytical protocol are not changed without a guarantee that this has no undesirable effects.

4. FURTHER READING

Calibration of Chemical Analyses and Use of Certified Reference Materials - Guide ISO-REMCO 32.

Quantifying Uncertainty in Analytical Measurement - EURACHEM Guide, (March, 1995).

Handbook for SRM Users - NBS Special Publication 260-100.

The International Laboratory Accreditation Cooperation (ILAC) is the principal international forum for the exchange of ideas and information on laboratory accreditation.

Established in the late 1970s, ILAC membership has grown rapidly and includes representatives from the world's major laboratory accreditation systems in Europe, Asia, North America, Australia and the Pacific. Countries that are developing their own laboratory accreditation systems are also welcome to participate and contribute.

ILAC operates a series of committees which investigate issues such as the harmonisation of international laboratory accreditation practices, the effectiveness of mutual recognition agreements in facilitating trade and the promotion of the aims and awareness of laboratory accreditation around the world.

There are regular meetings of individual ILAC committees as well as a major plenary meeting of all ILAC members.

The activities of ILAC affect a diverse range of areas including standardisation, accreditation, certification, testing, calibration, and regulation in both the public and private sectors.

ILAC Publications Currently Available

Information Documents (I Series)

ILAC-I1:1994	Legal Liability in Testing
ILAC-I2:1994	Testing, Quality Assurance, Certification and Accreditation
ILAC-I3:1996	The Role of Testing and Laboratory Accreditation in International Trade
ILAC-I4:1996	Guidance Documents for the Preparation of Laboratory Quality Manuals

Guidance Documents (G Series)

ILAC-G2:1994	Traceability of Measurement
ILAC-G3:1994	Guidelines for Training Courses for Assessors
ILAC-G4:1994	Guidelines on Scopes of Accreditation
ILAC-G7:1996	Accreditation Requirements and Operating Criteria for Horseracing Laboratories
ILAC-G8:1996	Guidelines on Assessment and Reporting of Compliance with Specification
ILAC-G9:1996	Guidelines for the Selection and Use of Certified Reference Materials
ILAC-G10:1996	Harmonised Procedures for Surveillance & Reassessment of Accredited Laboratories
ILAC-G11:1998	Guidelines on Assessor Qualification and Competence
ILAC-G12:2000	Guidelines for the Requirements for the Competence of Reference Material Producers
ILAC-G13:2000	Guidelines for the Requirements for the Competence of Providers of Proficiency Testing Schemes
ILAC-G14:2000	Guidelines for the Use of Accreditation Body Logos and for Claims of Accreditation Status
ILAC-G15:2001	Guidance for Accreditation to ISO/IEC 17025

Secretariat Documents (S Series)

ILAC-S1:2000	Guidelines for the Preparation, Layout and Numbering of ILAC Publications
ILAC-S2:1998	Rules

Procedural Documents (P Series)

ILAC-P1:2000	ILAC Mutual Recognition Arrangement (Arrangement): Requirements for Evaluation of Accreditation Bodies
ILAC-P2: 2000	ILAC Mutual Recognition Arrangement (Arrangement): Procedures for the Evaluation of Regional Cooperation Bodies for the Purpose of Recognition