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## Reference Materials in Analytical Chemistry

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### Overview

- Definition
- Statement of purpose
- Role of reference materials in the field of chemical metrology
- Requirements for CRM
- General challenges in the preparation and certification of CRM
- Preparation of CRM
- Selection criteria of CRM
- Use of CRM
- Traceability of measurement through use of CRM
- Sources of information

## Definition of CRM

- A 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 realisation of the unit in which the property values are expressed and for which each certified value is accompanied by an uncertainty at a stated level of confidence.

## Statement of purpose

Any analytical measurement should be reliable and invariant

- in time
- in space
- method independent
- analyst independent

Realized by standardisation, harmonisation and assuring the quality of measurements

## Statement of purpose

- The goal of any analytical measurement is to get accurate, reliable and consistent data
- Prerequisites for achieving accurate results:
  - Correct sampling
  - Correct weighing of the samples and standards
  - Use of well maintained and calibrated equipment
  - Qualify operators
  - Validated methods and procedures
  - Use of accurate standards or certified reference materials

- Reference materials provide the benefit of comparability between results obtained at different times, in different places, by different analysts, and using different methods.

When is an analytical result acceptable ?

The result is acceptable when  
it has been obtained by an established method

- All the uncertainties (systematic and random) have been taken into consideration in the uncertainty value being quoted

- the method used has been validated by analysing a known secondary (working) reference material
- The method used has been calibrated with a known certified reference material whose value is traceable to international metrological unit

## The role of certified reference material

- Certified reference materials (CRM) (i.e., with a statement of uncertainty and traceability), when available and of suitable composition, are ideal control materials.
- Regarded for traceability purposes as ultimate standards of trueness
- In the past CRMs were regarded as being for reference purposes only and not for routine use.
- A more modern approach is to treat CRMs as consumable and therefore suitable for IQC.
- The use of CRMs in this way is, however, subject to a number of constraints

## The role of certified reference material

- (i) Despite the constantly increasing range of CRMs available, for the majority of analyses there is no closely matching CRM available.
- (ii) Although the cost of CRMs is not prohibitive in relation to the total costs of analysis, it may not be possible for a laboratory with a wide range of activities to stock every relevant kind of reference material.

## The role of certified reference material

- (iii) The concept of the reference material is not applicable to materials where either the matrix or the analyte is unstable.
- (iv) CRMs are not necessarily available in sufficient amounts to provide for IQC use over extended periods.
- (v) It must be remembered that not all apparently certified reference materials are of equal quality.
- Caution is suggested when the information on the certificate is inadequate.

- **Primary standard:** Material designated or widely acknowledged as having the highest metrological qualities and whose value is accepted without reference to other standards of the same quantity.
- e.g uranium metal or plutonium metal.
  
- **Secondary standard:** Material whose values is assigned by comparison with a primary standard of the same quantity.
- eg.uranium dioxide pellets or plutonium oxide. Their reference value is assigned by comparison with the respective metal standard.

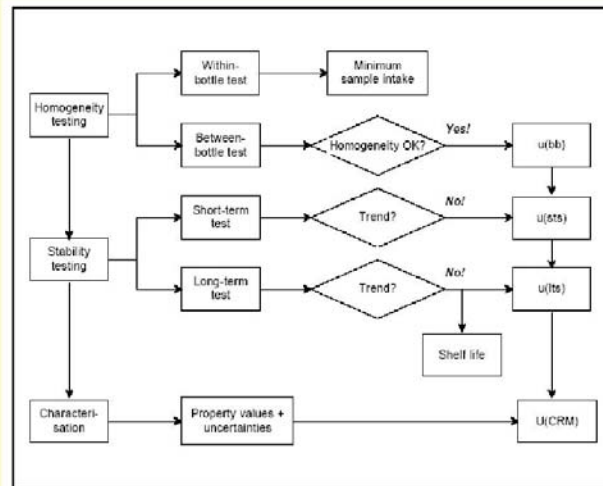
- **Working standard:** Used routinely to calibrate or check materials measured, measuring instruments or reference materials.  
e.g . Mercury standards prepared in-house.
- **Certified Reference Material (CRM) :** A reference material accompanied by a certificate one or more of whose properties are certified by a procedure which establishes traceability to an international unit of metrology.
- The certified value is accompanied by an uncertainty a stated level of confidence.

## Requirements for certified reference material

- The compounds and concentration should be similar as possible to the unknown sample.
- The material should be 'matrix matched'. Unfortunately full matrix matching frequently is an unrealistic requirement.
- The reference material should be homogeneous ( homogeneity test)
- If there is a risk for segregation during transport or storage the material must be re-homogenized before use.

- The certified properties of the reference material and the matrix should be stable.
- The material should be checked for stability as part of the verification process
- The uncertainty of the value should be estimated for certified reference materials.

## Certification CRM



## General Challenges in the Preparation and Certification

- Reference materials (RMs) serve as the basis for millions of measurements performed each year.
- The “reliability” of these materials, the associated reference value and the stated uncertainty are of key importance.
- A high degree of confidence needs to be put in the measurements and in the reference materials.
- Preparation and certification of reference materials is a very demanding task. It requires a thorough understanding of the demanding task. It requires a thorough understanding of the processes involved.



## Preparation of Reference Materials

- 1. Definitive method  
The method must be based on first, principles have very high precision and essentially zero systematic error.
- An example is the use of isotope dilution mass spectrometry for the characteristics of trace level elements in natural matrix elements. The certification is done in a single laboratory

### Methods identified as having the potential to be primary

- Isotope dilution with mass spectrometry (IDMS)
- Coulometry
- Gravimetry (a) gas mixtures and b) gravimetric analysis
- Titrimetry
- Determination of freezing-point depression
- Measurements of amount of substance to be considered primary must be made using method which is specific for a defined substance and for which the values of all parameters or corrections which depend on other species or the matrix are known or can be calculated with appropriate uncertainty.

## Preparation of Reference Materials

### 2. Independent measurement method

Two or more reliable independent methods are used. The method must be proven to give accurate results. The certification is done in a single laboratory.

### 3. Interlaboratory consensus method

A number of laboratories analyze in replicate one or more units of the material being characterized. The participating laboratories may choose their own method or all laboratories may use the same method. The consensus value is usually taken as the mean

## Selection Criteria for CRMs

- A reference material is selected by comparing the uncertainty contribution of the reference material ( $I_r$ ) to the total analytical uncertainty ( $I_T$ ) and by evaluating this as satisfactory, acceptable or incompatible.

$I_T/I_r > 10$ : 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

$I_T/I_r < 2$ : Unsatisfactory situation; implies reviewing the total uncertainty, the method, applied and the choice of reference material

## Use of Reference Materials

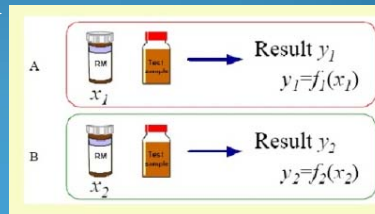
- (a) Method Validation and Measurement Uncertainty
  - Bias estimation, one of the most difficult elements
  - Appropriate RMs provide information within the limits of the uncertainty in certified value(s) and the uncertainty of the method
- (b) Verification of the Correct Use of a Method
  - RM can be used for training purpose
  - For checking infrequently used methods
  - For trouble shooting when unexpected results are obtained.

## Use of Reference Materials

- (c) Calibration
  - Normally a pure substance RM is used for calibration
  - Other components such as sample digestion, separation and derivatisation are not covered.
  - The uncertainty associated with RM purity will contribute to the total uncertainty of the measurement.

## Traceability of the measurements

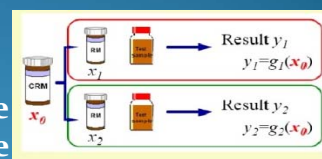
Consider two laboratories A and B carrying out measurements on samples of broadly the same type. Each calibrates their equipment using a reference standard with a known nominal concentration ( $x_1$  and  $x_2$  respectively). They calculate their respective results  $y_1$  and  $y_2$  from an equation calibration including the respective values of values of  $x$



## Traceability of the measurements

If, however the two reference standards are both calibrated against some **common reference, a comparison becomes meaningful**. Now, both results are derived from the same value ( $x_0$ ). Both will now have the same units of units of measurements (same scale and units as  $x_0$ ), and a direct comparison of the values  $y_1$  and  $y_2$  is now not only possible but also meaningful.

By analogy of course,  $x_0$  could also be derived from a yet higher reference to allow global comparisons.



## Traceability of the measurements

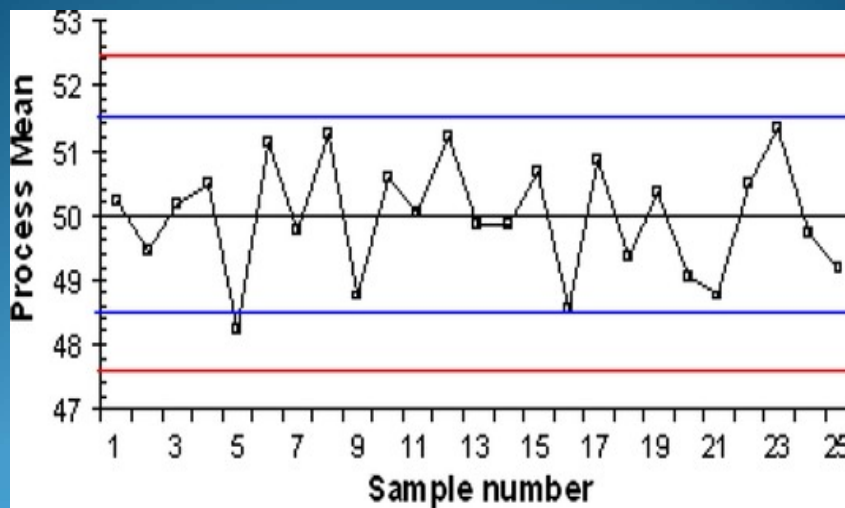
- **Primary Standards**  
Certified by nationally or internationally recognized institutes (NIST, BCR, NIMB)
- **Secondary (certified) standards**  
 Traceable back to Primary Standards or otherwise verified, for example through independent test method, with certificate from manufacturer (Supelco, Fluka)
- **Working Standards**  
 Prepared by user with traceability to Primary or Secondary standards or otherwise verified, for example through independent test method



## Used of certified reference materials

- Control charts and reference materials:  
 -Demonstration of measurement procedure performing within given limits.  
 (Warning limits and Control limits)
- If the control value is outside the limits, no analytical results are reported and remedial actions have to be taken to identify the sources of error and to remove such errors.

## Example of control chart



## Examples of CRMs



## Sources

- (1) K.L. Ramakumar  
Bhabha Atomic Research Centre Mumbai 400 085  
[Klram@barc.gov.in](mailto:Klram@barc.gov.in)
- (2) Papadakis, I.: ( Certified Reference Materials)  
In: Wenclawiak, Koch, Hadjicostas (eds.)

THANK YOU