

# CHARACTERIZATION STUDIES OF THE CANDIDATE REFERENCE MATERIALS

**Aida Jotanović;**

**Institute of metrology of Bosnia and Herzegovina**

***(Presented by Süleyman Can (TÜBİTAK UME))***

## CONTENTS:

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- Evaluation of proper value
- Certification

## DEFINITIONS:

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### ➤ 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.

### ➤ CERTIFIED REFERENCE MATERIAL (CRM)

Reference material accompanied by documentation issued by relevant body and provide one or more specified property values with associated uncertainties and a statement of traceability, characterized by a metrological valid procedure.

## DEFINITIONS:

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➤ PRODUCTION OF REFERENCE MATERIAL

All necessary activities and tasks leading to a reference material.

➤ CANDIDATE REFERENCE MATERIAL

Material intended to be reference material.

➤ CHARACTERISATION OF CANDIDATE REFERENCE MATERIAL

Value assignment – The estimation of the mean value of quantity of candidate material.

## GENERAL

- Characterization of candidate reference material is in general process of determination of assigned value for specific measurand.
  
- There are two main approaches:
  1. Characterization by a single method
  2. Characterization by multiple methods and/of multiple laboratories

*NOTE: Both approaches should be able to make their measurements traceable to the references*

## GENERAL

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- An appropriate approach can be chosen depending on:
  - The type reference material
  - Knowledge of the specific matrix
  - End-use requirements
  - Qualifications laboratory involved
  - Quality of method(s) / Measurement capabilities
  - Ability to estimate the uncertainty
  - Intended use of the material

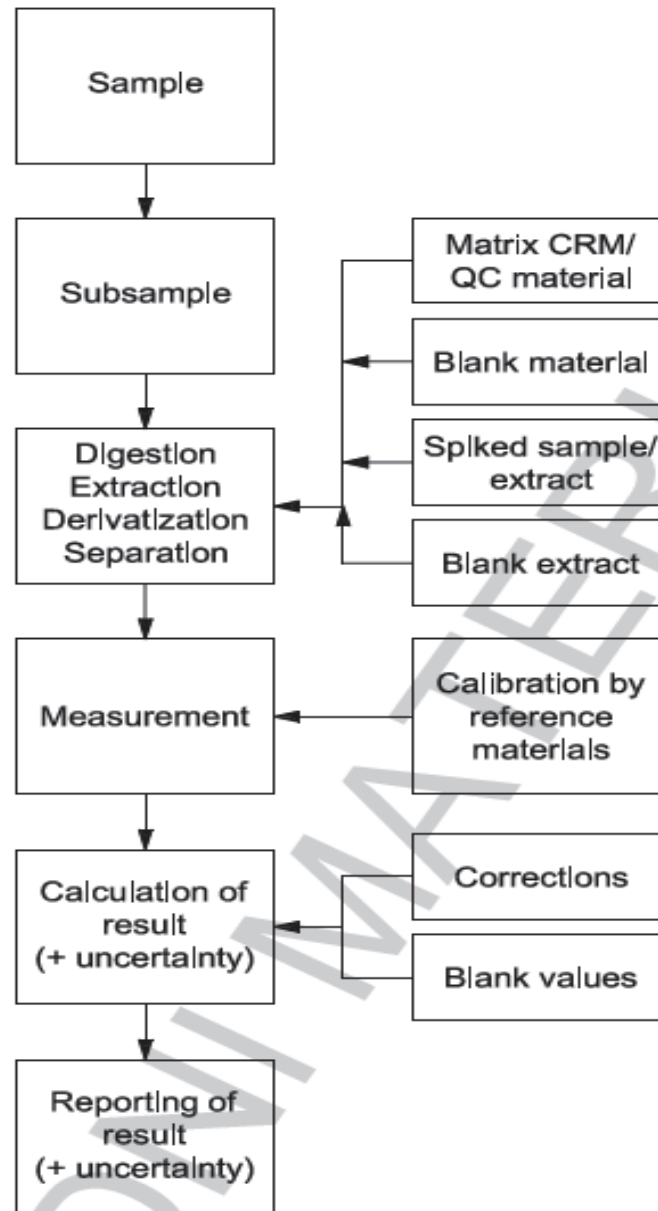
*NOTE: Each approach requires a good knowledge of statistical modeling of data*

## GENERAL

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- Establishing and demonstrating traceability is important requirement of reference material in its role as a measurement standard.
  
- There are several possibilities for achieving traceability:
  - Property values should be made traceable to SI units and expressed in corresponding units

# ESTABLISHING AND/OR VERIFYING TRACEABILITY





## GENERAL

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- Property values can be made traceable to standard method and/or SOPs developed on the basis of the standard methods
- Property values can be made traceable to other measurement standards of artifacts, including CRMs and RMs

*NOTE: Choosing approach should be made based on the intended use of the CRM*

## APPROACH 1: *single method in one laboratory*

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- Includes experimental set-ups known as *collaborative study*
- Used measurements procedures should be made traceable to (preferably) SI units
- Group of measurement methods that can be used is formed by primary methods of measurement

## APPROACH 1: *single method in one laboratory*

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### CCQM DEFINITION:

- Primary methods of measurement is a method having the highest metrological properties, whose operation can be completely described and understood for which a complete uncertainty statement can be written down in terms of SI units.
- Primary direct method measures the value of unknown without reference to a standard of the same quantity.
- Primary ratio method measures the value of ratio of unknown to a standard of the same quantity.

## APPROACH 1: *single method in one laboratory*

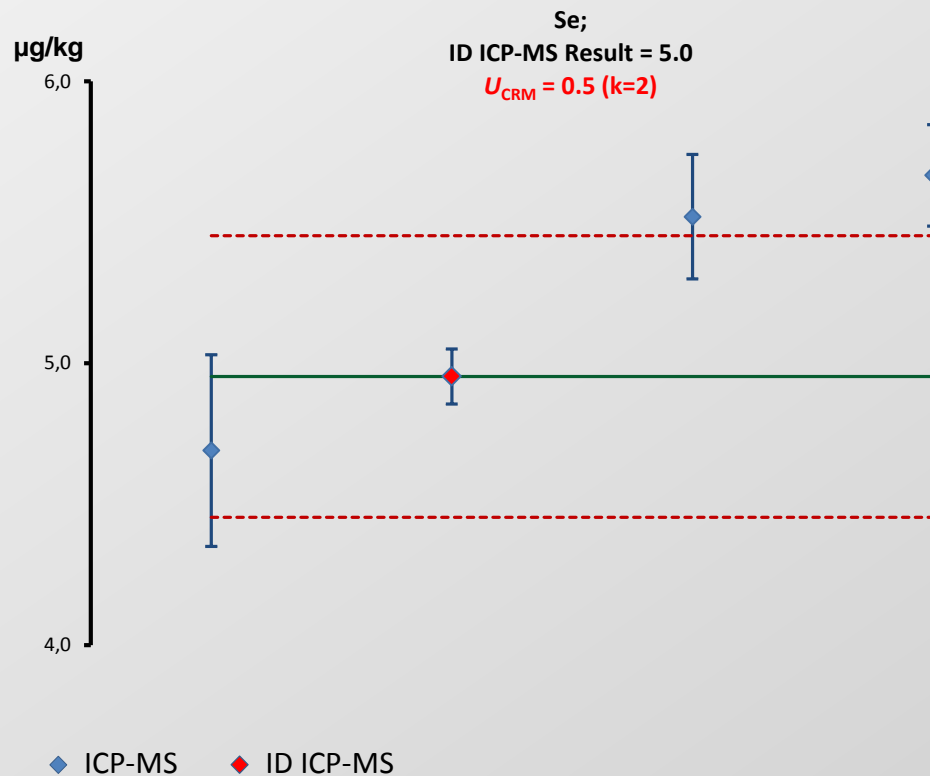
*CCQM has identified several methods with potential of being primary methods of Measurements*

- Isotope dilution with mass spectroscopy
- Coulometry
- Gravimetry
- Titrimetry
- $k_0$  Instrumental Neutron Activation Analysis ( $k_0$ -INAA)

## APPROACH 1: *single method in one laboratory*

- ENVCRM 01 – Elements in River Water CRM

Se characterization value



## APPROACH 2: *one or more methods in multiple laboratory*

- The concept of determination based on agreement among method(s) and/or laboratories is based on:
  - There exist a population of methods and laboratories that is capable in determination of characteristics of the RM to provide results accurate enough
  - The differences between individual results, both, within and between methods/laboratories are statistical regardless

## APPROACH 2: *one or different methods in multiple laboratory*

➤ The general procedure for the characterization of a candidate reference material using Approach 2 can be described as follows:

- Preparation of the material
- Stability and homogeneity testing
- Sending the proper amount of candidate material to laboratories

*This step includes providing to participants the clear instructions regarding storage of sample, number of measurement (ect)*

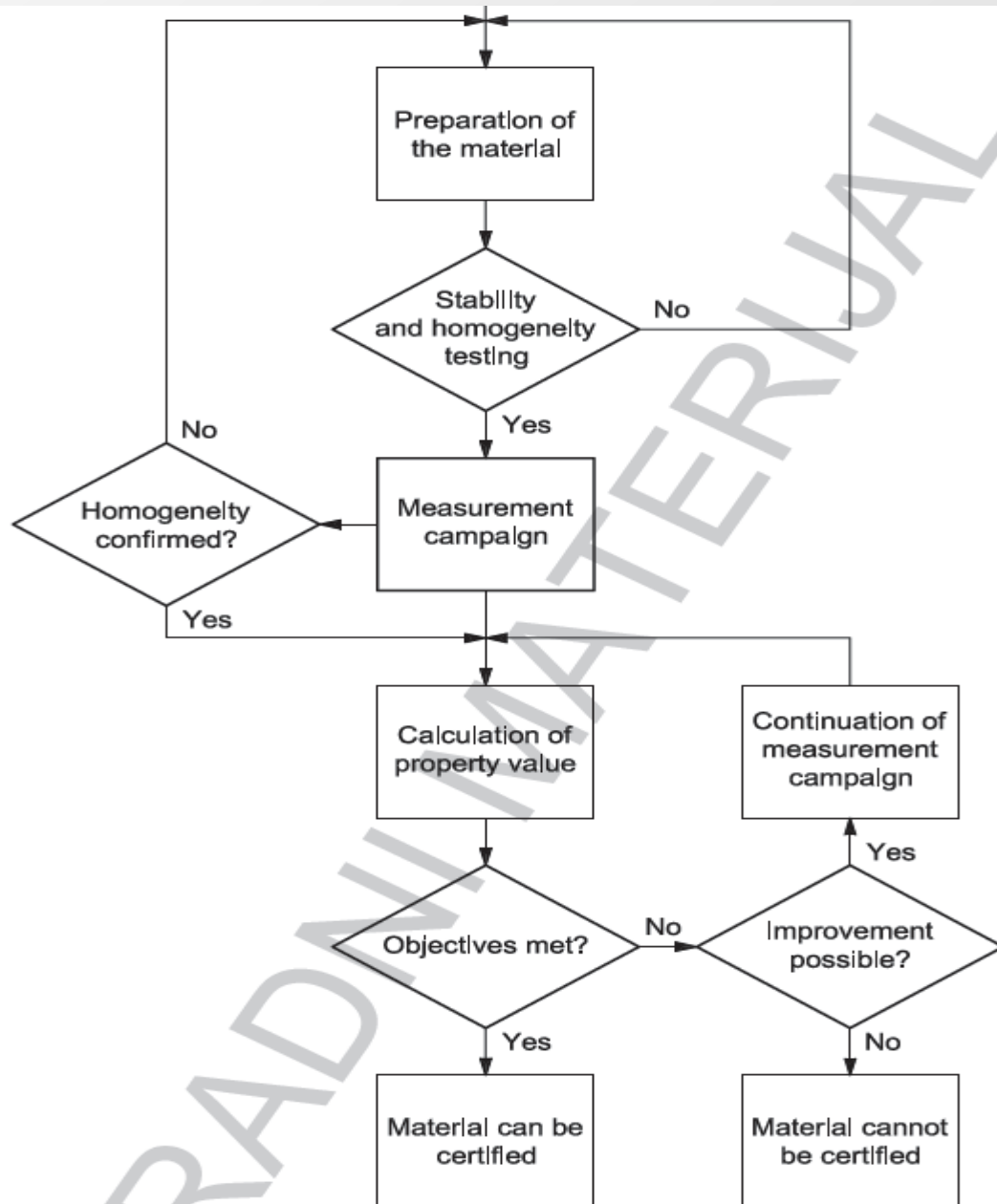
## **APPROACH 2: *one or different methods in multiple laboratory***

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- Collecting the results
- Estimation of assigned value and measurement uncertainty
- Certification of material



## APPROACH 2 - SHEMATICALLY

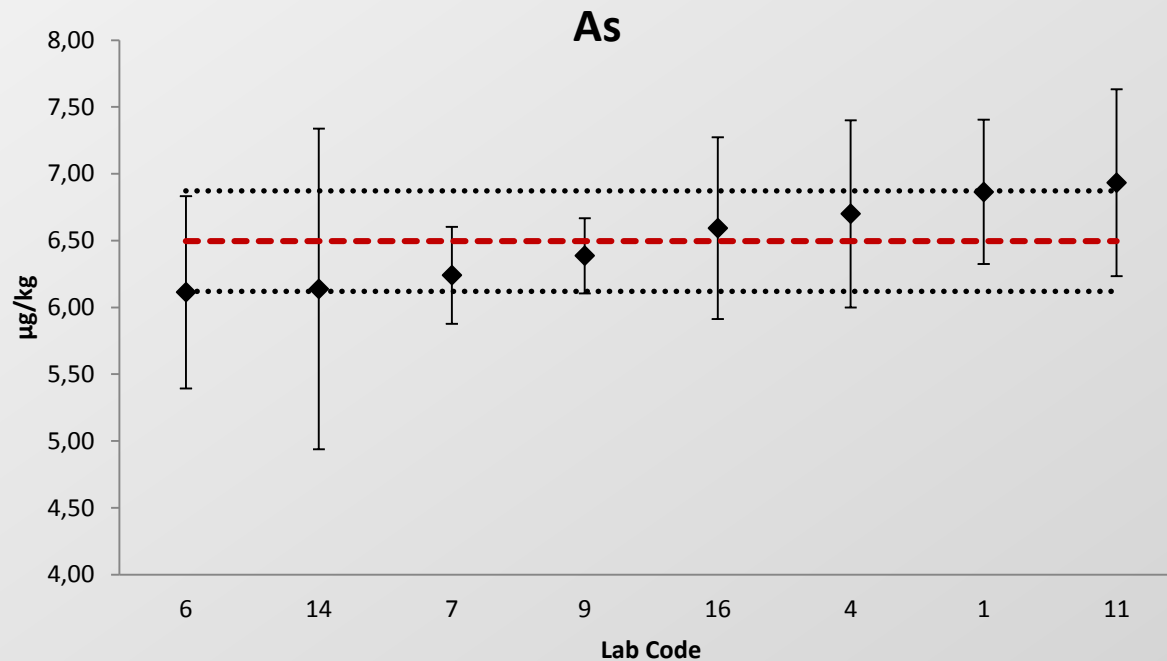


## APPROACH 2: *one or different methods in multiple laboratory*

- Results from different methods should be checked in order to see whether they agree within uncertainties.
- The minimum number of participating laboratories in the characterization study is variable, depending on complexity of the measurement procedure.
  - Well established methods – the number can be small as 2 or 3
  - The more complex procedure, the larger between laboratory variation can be expected – increase the number of laboratory

## APPROACH 2: *one or different methods in multiple laboratory*

➤ UME CRM1201 – Elements in Spring Water CRM



### **APPROACH 3: *two or more reference methods in one laboratory***

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- Each technique should be validated and metrologically traceable.
- Results from different methods should be checked in order to see whether they agree within uncertainties. Bias tests should be performed.
- Combination of primary and conventional methods is possible.

## **APPROACH 4: *method dependent measurement results***

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- The measurand is a parameter measurable with certain protocol (e.g. International standard) or an operational procedure.
- Traceability of measurements is still very important.
- Method dependent certification.

## STATISTICAL EVALUATION OF DATA

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### Approach 1: single method in one laboratory

- The assigned value should be average from a designed study using more than one items of candidate reference material and after applying appropriate outlier tests using suitable measurement method.

Appropriate measurement method is previously explained!

## STATISTICAL EVALUATION OF DATA

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### Approach 1: single method in one laboratory

- The assigned value should be estimated under more than one measurement conditions.

Different time of measurement, analyst, etc.!

- The assigned value should be estimated using sufficient number of replicate measurements.

Series of repeated test on each candidate material item!

## STATISTICAL EVALUATION OF DATA

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### Approach 2: one/multiple method in multiple laboratory

- The assigned value can be determined using interlaboratory comparison study.
- The assigned value is the estimate of robust mean, median or arithmetic mean, calculated using appropriate procedure.
- Each laboratory is required to provide a standard uncertainty with their results.



## STATISTICAL EVALUATION OF DATA

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### Approach 2: one/multiple method in multiple laboratory

#### ➤ MEDIAN

- statistical technique robust to outliers
- estimator of the population mean for symmetric distribution

To determine median:

- Sort data into increasing order
- Calculate:

## STATISTICAL EVALUATION OF DATA

### Approach 2: one/multiple method in multiple laboratory

- Middle of a sorted series of data (odd No. of laboratories)
- Average of the two middle values of a sorted series of data (even No. of laboratories)

$$\text{med}(x) = \begin{cases} x_{\{(p+1)/2\}} & p \text{ odd} \\ \frac{x_{\{p/2\}} + x_{\{1+p/2\}}}{2} & p \text{ even} \end{cases}$$

## STATISTICAL EVALUATION OF DATA

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### Approach 2: one/multiple method in multiple laboratory

#### MAD - Median of absolute deviations

- Robust standard deviation
- Estimate of the population standard deviation for normally distributed data

## STATISTICAL EVALUATION OF DATA

### Approach 2: one/multiple method in multiple laboratory

To estimate MAD:

- Calculate absolute differences

$$d_i = |x_i - \text{med}(x)|$$

*MAD = median of absolute differences*

- Calculate MADe:

$$\text{MADe}(x) = 1,483 \text{ med}(d)$$

## STATISTICAL EVALUATION OF DATA

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### Approach 2: one/multiple method in multiple laboratory

#### ➤ CONSENSUS VALUE: ISO 13528 algA

- Statistical technique robust to outliers
- Robust estimates of the mean and standard deviation of the data

To estimate robust mean and std:

- Sort data into increasing order

## STATISTICAL EVALUATION OF DATA

### Approach 2: one/multiple method in multiple laboratory

- Use robust estimate of median and MADe
- Update values as follows:

$$x^* = \text{median of } x_i \quad (i = 1, 2, \dots, p)$$

$$s^* = 1,483 \text{ median of } |x_i - x^*| \text{ with } (i = 1, 2, \dots, p)$$

- Recalculate  $x^*$  = ARITHMETIC MEAN
- Recalculate  $s^*$  arithmetic mean and 1.134s

## STATISTICAL EVALUATION OF DATA

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### Approach 2: one/multiple method in multiple laboratory

- The robust estimates of mean and standard deviations may be derived by an iterative calculation
- Process converges – there no change from one iteration to the next

## CERTIFICATION

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- CRM is accompanied by a certificate providing at least following:
  - Properties of interest
  - Their values
  - Their uncertainties
  - Statement concerning metrological traceability



## CERTIFICATION

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- Certificate accompanied a CRM is a summary of program of work, involving selection of material, assessment of homogeneity and stability, method of characterization, validity of the certificate, description of the sample, instructions for use, etc.

Questions?

Thank you for your attention!

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### Vijesti



**IMBİH - pridruženi član BIPM-a**

opširnije



**Najava - IMBİH domaćin 5-te Generalne skupštine EURAMET-a, Sarajevo 06.-09. juna 2011. godine**

opširnije



**Svjetski dan mjeriteljstva 2011.**

opširnije



**IMBİH na novoj lokaciji, ulica Augusta Brauna br. 2**

opširnije



**VAŽNO!! Preseljenje IMBİH-a u nove prostorije, ulica Augusta Brauna br. 2**

opširnije



**Privremeni prestanak rada Laboratorije za plemenite metale i referentne materijale IMBİH-a**

opširnije

### Odabrani sadržaj

**konverzija mjernih jedinica**



**Mjeriteljstvo/Metrologija**  
 ukratko, treće izdanje  
 Infrastruktura kvaliteta - Edukativni video (IFK)  
 Mjeriteljski sistem BiH  
 Konvencija o metru  
 Istorijat mjeriteljstva u BiH

### Međunarodna konferencija o mjeriteljstvu u BiH na njenom putu ka integraciji u EU









**IMBİH...**

- Pridruženi član BIPM od 2011. godine
- Posmatrač u IAAO od 2010. godine
- Certifikat ISO 9001:2008 od 2010. godine
- Posopravni član EURAMET od 2009. godine
- Pridruženi član WELMEQ od 2009. godine
- Pridruženi član OIML od 1997. godine