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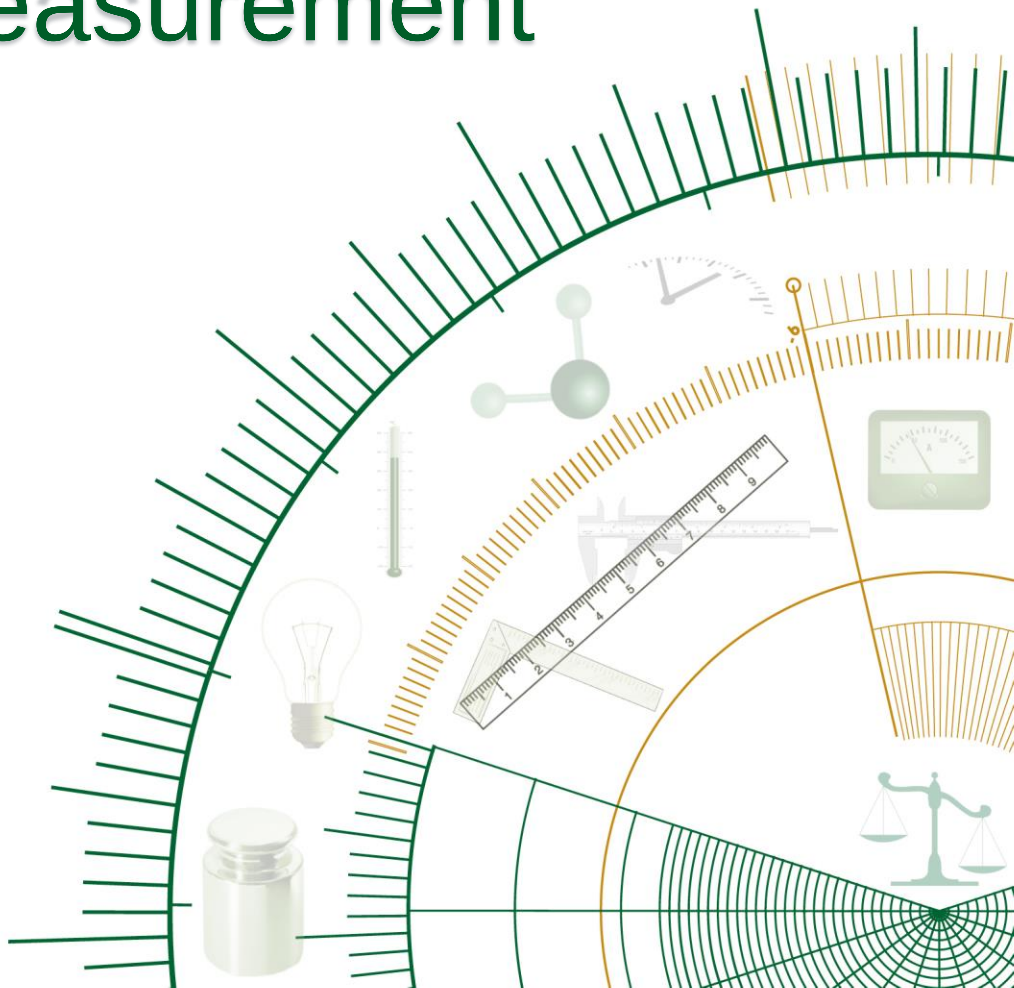
National Metrology Institute of South Africa

Traceability in Measurement



Maré Linsky

SADCWATER PT 2019 Workshop

MAHE, SEYCHELLES

18 – 20 NOVEMBER 2019

Your measure of excellence

Overview

- What is Metrological Traceability and why do we need it?
- Establishing traceability
  - Identification of measurand, measurement equation and influence quantities
  - Identify relevance of individual influence quantities to establish degree of control required
  - Choosing suitable references
  - Uncertainty associated with measurement
- Conclusions

Metrological Traceability

- Why do we need to metrological traceability?

Metrological Traceability

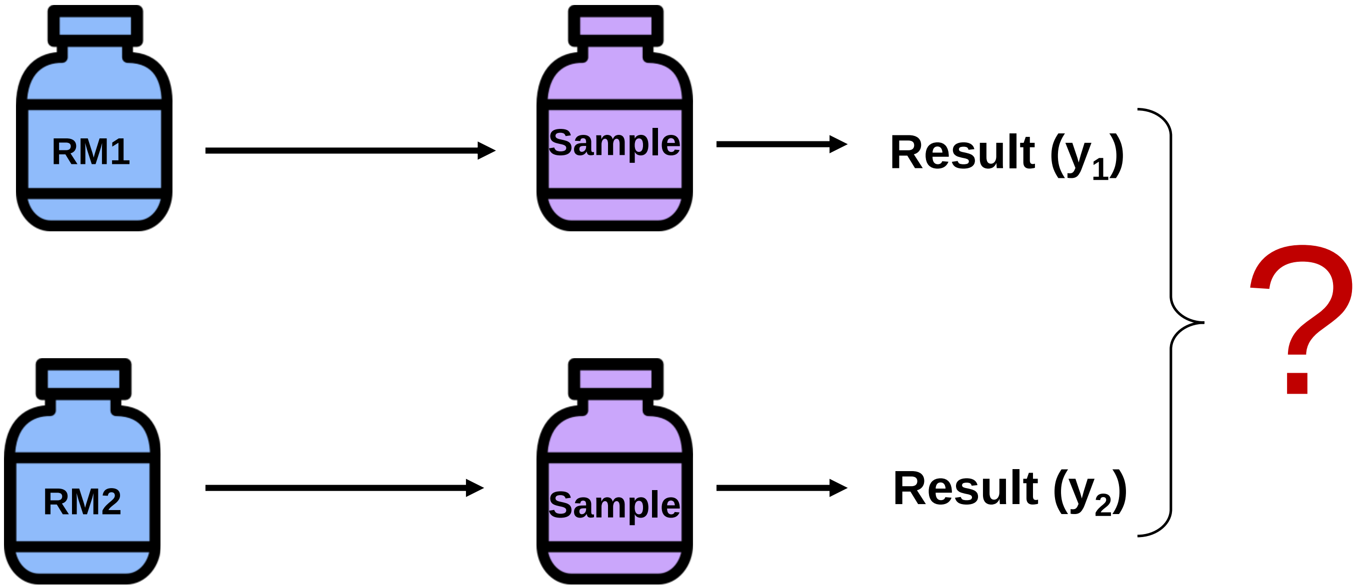
- Every day, thousands of chemical measurements support decisions on food safety, health and environmental protection

- The global market, too, needs accurate and reliable measurements so that technical barriers to trade can be minimised

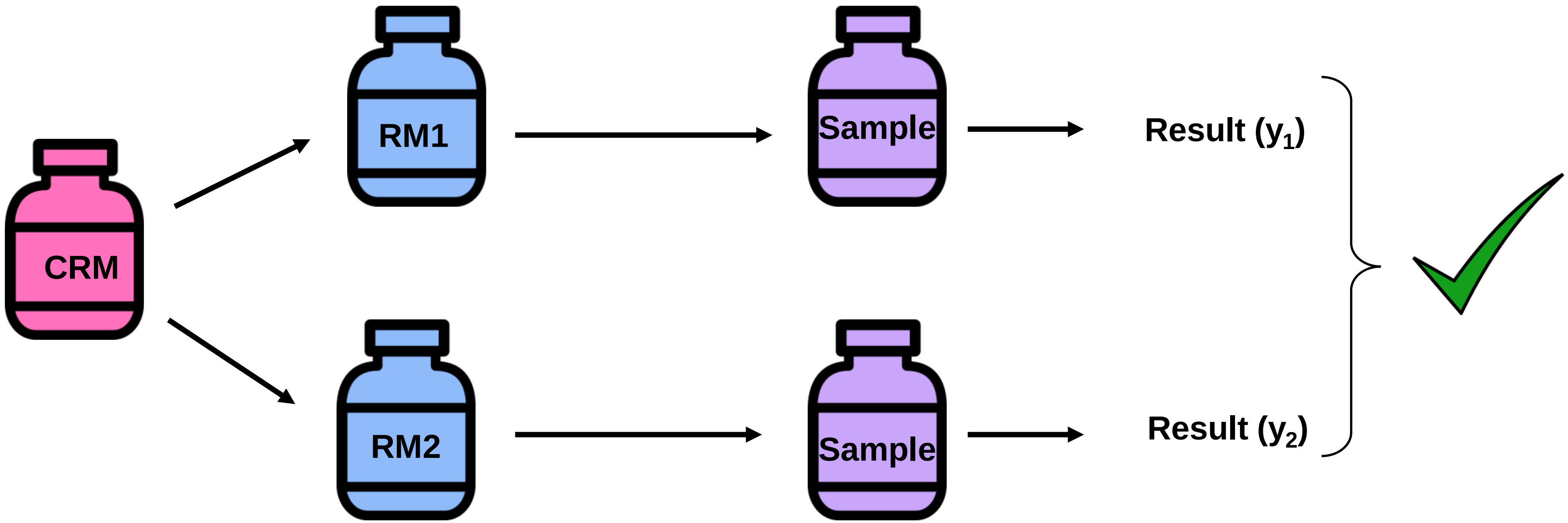
- Metrological traceability is key to ensuring the comparability of measurement results over time and between locations

Consistent measurement results?

…over time and between locations…



Consistent measurement results?



Results traceable to CRM

Traceability to the SI – if CRM traceable to SI

Metrological Traceability

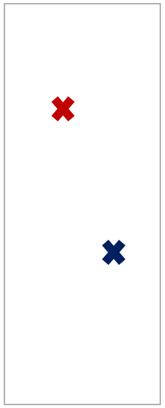
- Result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty

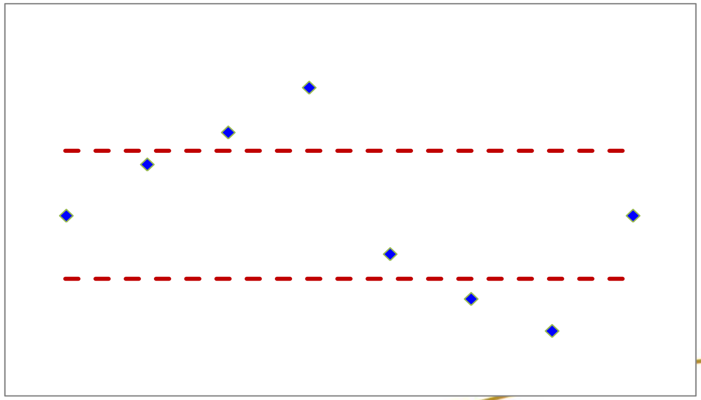
OR…

- Comparability through traceability to consistent and agreed set of measurement units and scales, i.e. SI

Why is Measurement Uncertainty Important?

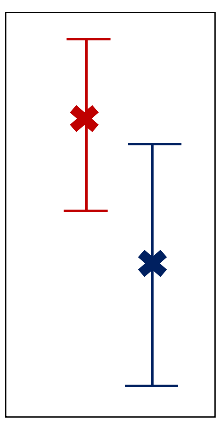
- "..unbroken chain of calibrations, each contributing to the measurement uncertainty.."
- Many important decisions are based on the results of chemical quantitative analysis
  - To check materials against specifications or statutory limits
  - To estimate monetary value

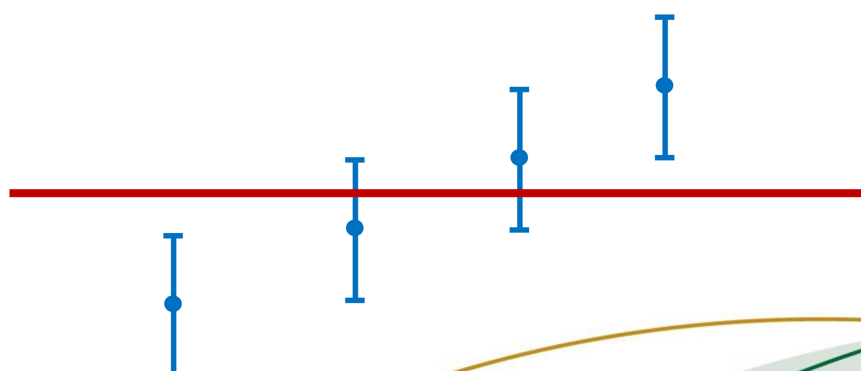




Why is Measurement Uncertainty Important?

- Parameter, associated with the result of a measurement, that characterises the spread of values that could reasonably be attributed to the measurand (GUM)
    - Measurement uncertainty is a key figure in the decision of whether an analytical result is fit for the customers purpose





Establishing metrological traceability

- The traceability of measurement results is usually ensured through proper calibration of all relevant input quantities against appropriate measurement standards and/or certified reference materials

General traceability concepts

$$y = f(x_1, x_2, \ldots x_m)|_{x_{m_+1}, x_{m_+2} \ldots x_n}$$

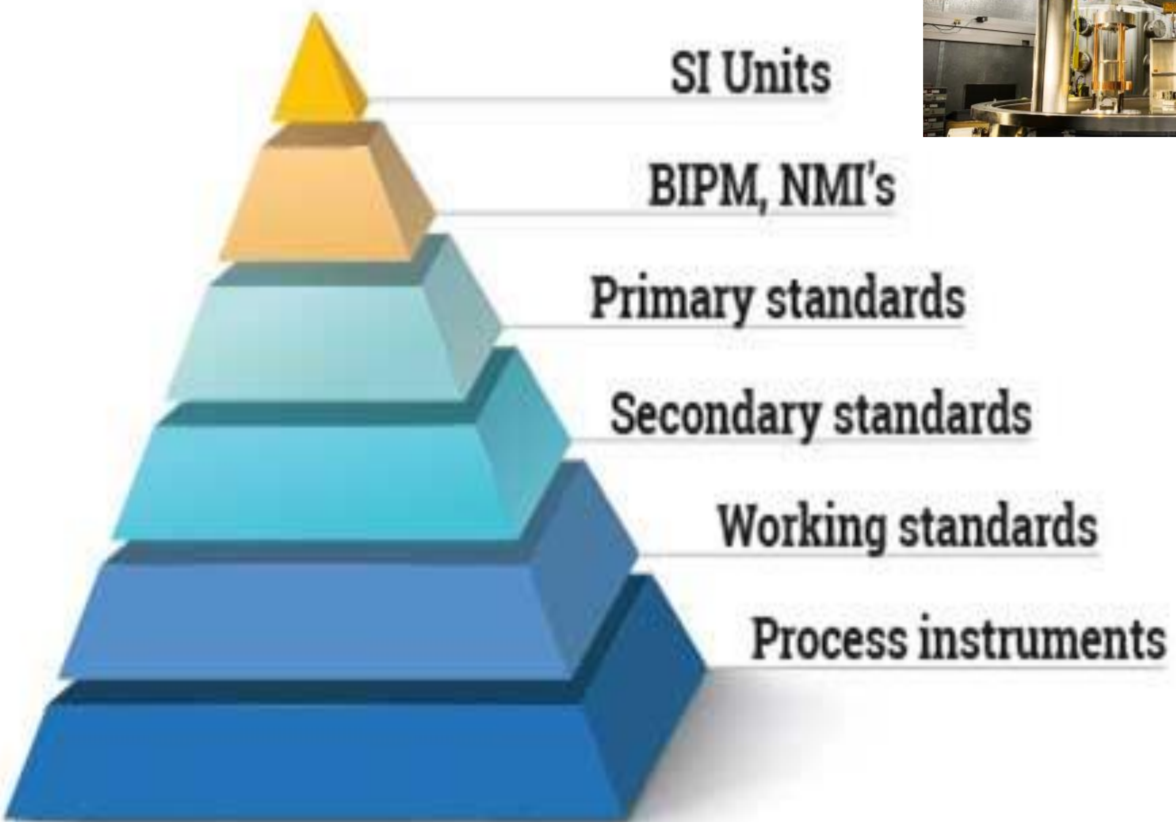
- Measurand (y) traceable to x_1 to x_n
  - Influence quantities could be related to:
    - Fixed conditions, e.g. Extraction time, Extraction solvent, Time
    - Variable conditions, e.g. Mass, Volume, Concentration
  - $x_1 - x_n$ should also be traceable / defined values
  - Note: Sufficient to ensure that $x_1 - x_n$ are under sufficient control to provide required uncertainty in y
    - For critical values – traceable calibration against reference values
    - For less critical values – less stringent control adequate

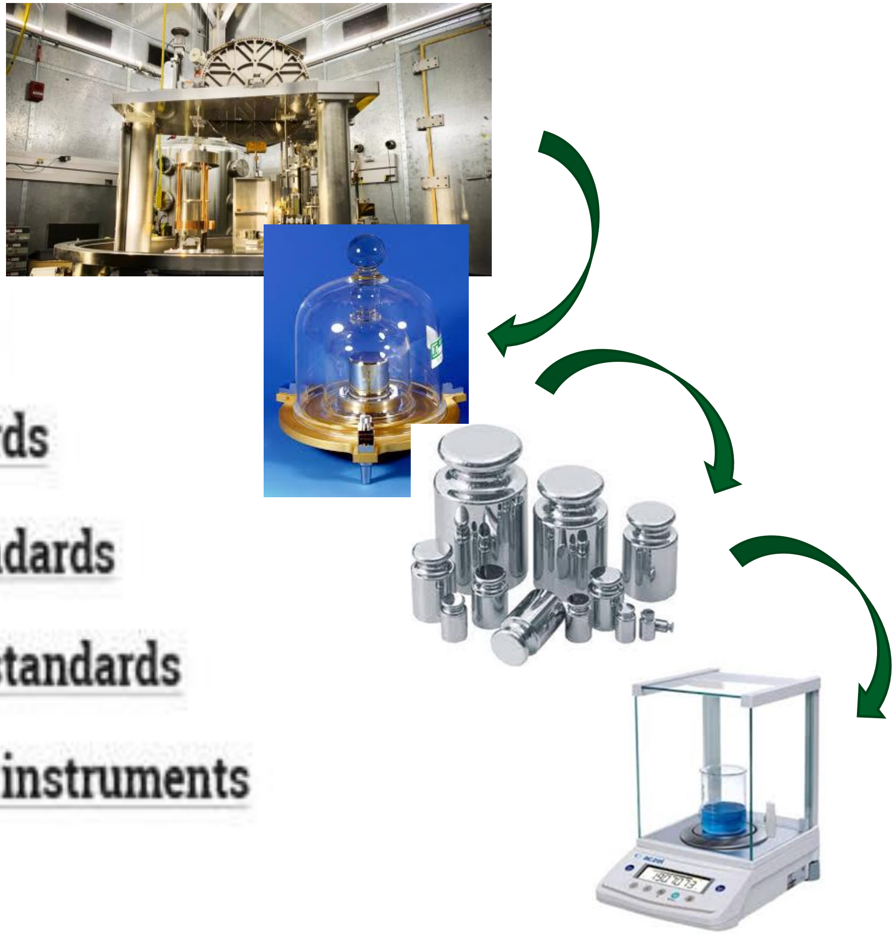
In a nutshell..

- Whether or not the measurand is operationally defined, the establishment of traceability requires the same activity; every quantity that materially affects the measurement result should be subject to calibration or should be kept under suitable control, usually by use of calibrated instruments

What does this mean?

Metrological Traceability





Metrological Traceability

How do we evaluate the Metrological Traceability of our results?

Key elements (main steps)

- Specifying measurand, scope measurement and target measurement uncertainty
- Choosing suitable method, including equation and measurement conditions
- Validation
- Identify relative importance of influence quantities
- Selection of appropriate measurement standards
- Estimation of uncertainty of measurement

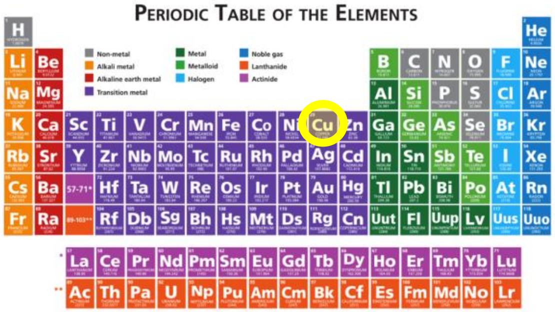
- Very abstract…

Example

- Prepare a 1000 mg/L Cu standard calibration solution (at 20 °C) with a required standard uncertainty of 2 mg/L (0.2%) or better.

Step 1: Specify measurand and target uncertainty

- Identity of analyte



- Target uncertainty
  - Uncertainty of the result cannot be better than any of the uncertainties of measurement standards used in method
    - Rule of thumb: Not more than 1/3 of target uncertainty
  - Smaller uncertainties require greater control of influence quantities / control of more variables

Step 2: Identify suitable method

- Standard Operating Procedure (SOP)
  - Fit for purpose
  - Equation / set of equations to calculate measurement result

$$y = f(x_1, x_2, \ldots x_m)|_{x_{m_+1}, x_{m_+2} \ldots x_n}$$

  - Measurement parameters (x_1 to x_m) and conditions (x_{m+1} to x_n) that should controlled during procedure

Step 1 & 2: Specify measurand and target uncertainty & Identify suitable method

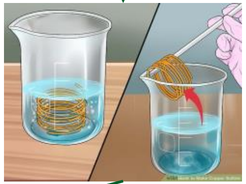
- Measurand: 1000 mg/L Cu standard calibration solution
- Target uncertainty ≤ 2 mg/L

Stock Calibration Std

OR

High purity metal

Pipette Std Aliquot



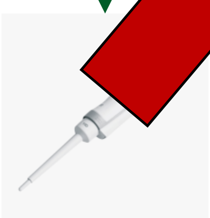
Dissolve metal

Dilute standard to final volume

Step 1 & 2: Specify measurand and target uncertainty & Identify suitable method

- Measurand: 1000 mg/L Cu standard calibration solution
- Target uncertainty ≤ 2 mg/L

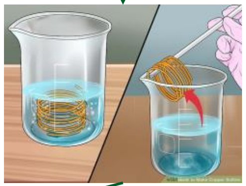
Stock Calibration



Pipette Std Aliquot

OR

High purity metal



Dissolve metal

Dilute standard to final volume

$$Conc(Cu)_{CalibStd} = \frac{P(metal) \times m(metal)}{V(Fin)}$$

Step 1 & 2: Specify measurand and target uncertainty & Identify suitable method

- Influence quantities

$$Conc(Cu)_{CalibStd} = \frac{P(metal) \times m(metal)}{V(Fin)} \quad at\ 20\ ℃$$

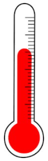
  - Mass high purity copper
  - Purity of copper
  - Final volume
  - Temperature

Step 3: Validation

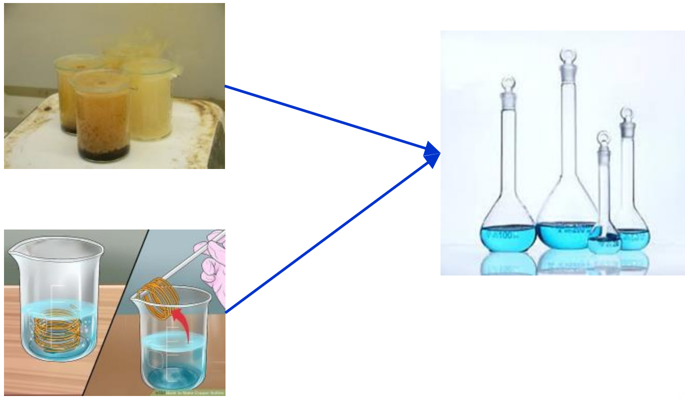
- Confirms that standard operating procedure is adequate (fit for purpose), i.e. all influence quantities (parameters and measurement conditions) have been correctly identified and controlled
- Critical to establish traceability

Step 3: Validation

- Preparation of a Cu Calibration standard
  - Influence quantities subject to calibration:
    - Mass
    - Volume
    - Purity
  - Influence quantities kept under suitable control, usually by use of calibrated instruments
    - Temperature
  - Incomplete dissolution?



Step 4:
Relative importance



Step 4: Relative importance of influence quantities

- Decision on appropriate level of control or calibration based on:
    - Quantitative effect on measurement result
    - Uncertainties associated with effect, i.e. uncertainty budget
- Critical: Variables from equation
    - Control through calibration
        - Example Cu Std: Mass, Volume and Purity

- Uncertain: Conditions from SOP
    - Robustness / Ruggedness study / investigation
        - Example Cu Std: Temperature (volume), Digestion time
- Typically easier to control physical effects (e.g. mass) than chemical effect (e.g. digestion)

Step 4: Relative importance of influence quantities

- Level of control required for temperature?
  - Would the worst-case scenario have a significant impact on the measurement result?

Temperature error (°C)	Concentration error (mg/L Cu)
10.0	2.00
5.0	1.00
2.0	0.4
1.0	0.2
0.1	0.02

?

$$\frac{0.4}{2.0} \times = 20\%$$

Target Uncertainty ≤ 2 mg/L

Step 5: Choosing and applying appropriate references

- To ensure that all values in the measurement equation, and all other fixed values specified / implied in the measurement, are traceable to appropriate references
- Establish procedures for:
  - Calibration of equipment measuring or controlling fixed values
  - Calibration, certification or control of all refences used

Step 5: Choice of reference

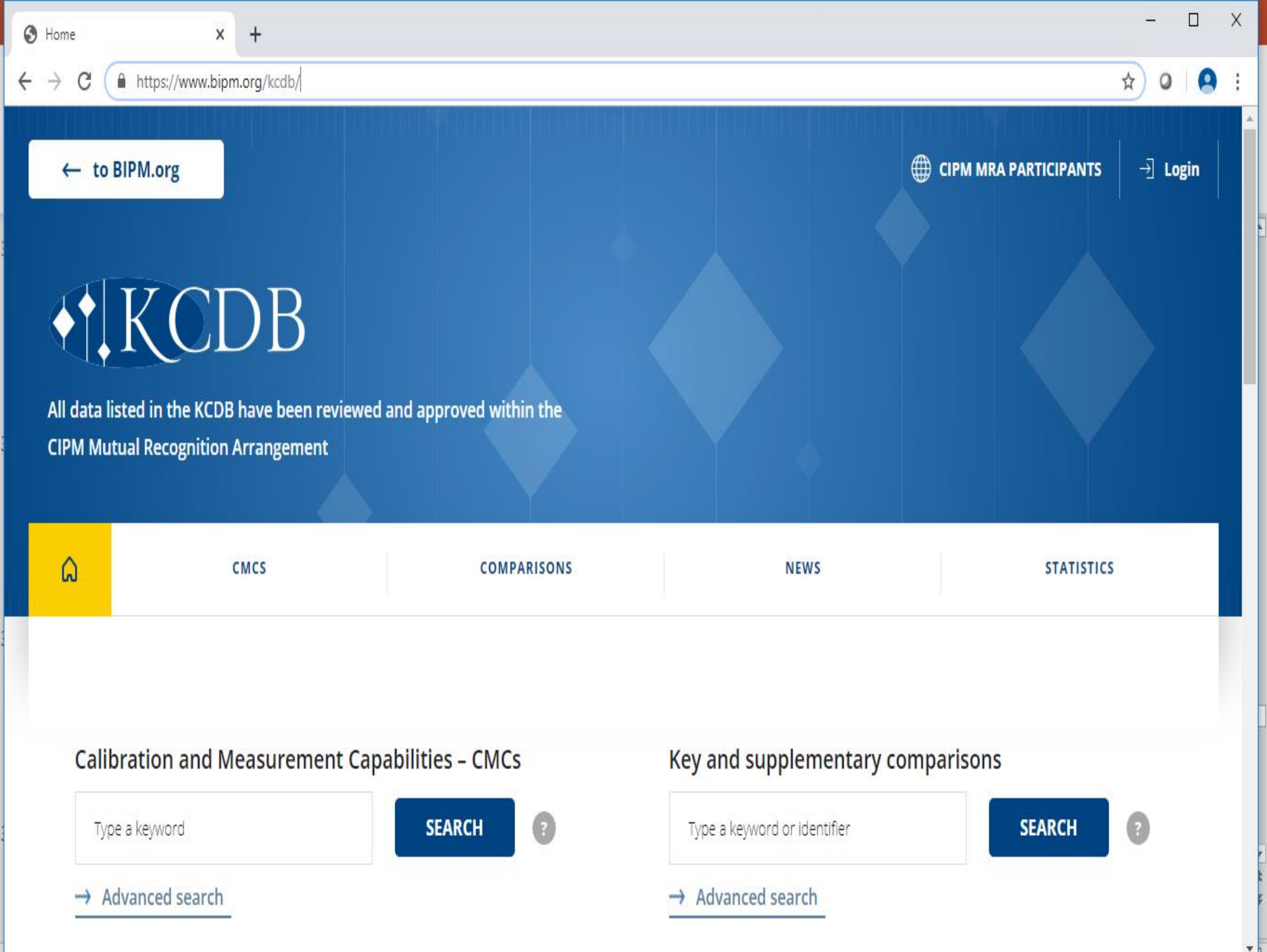
- Physical measurements
  - Calibration of equipment used for physical measurements (e.g. mass, volume) is typically well established
  - Associated with relatively small uncertainties

- Chemical measurements
  - Confirmation of identity
    - Certified reference materials (CRM)
      - Pure material
    - Reference data
  - Traceability to amount of substance (concentration)
    - Certified reference materials (CRM)
      - Pure material
      - Calibration solution standards
      - Matrix reference material

Certified Reference Material (CRM)_VIM 2

- A reference material, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures
  - Demonstrated traceability to national or international standards
  - Statement of uncertainty

National Metrology Institute:
https://www.bipm.org/kcdb/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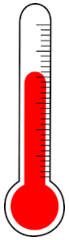
CRM Certificate

- Some requirements:
  - Title, name of RM, unique identifier
  - Name and contact details of RM producer
  - Property of interest, property value and associated uncertainty
    - Specify measurement method for method dependent measurands
  - Metrological traceability
  - Intended use
  - Instructions for handling and use, including minimum sample size (if applicable)
  - Storage information
  - Period of validity

Step 5: Preparation of a Cu Calibration standard

- Mass: Balance Calibration certificate (ISO 17025 calibration laboratory)
  - Extended calibration intervals, so validity can be confirmed with daily check weights, which is also traceable to national standards (i.e. calibration certificate)

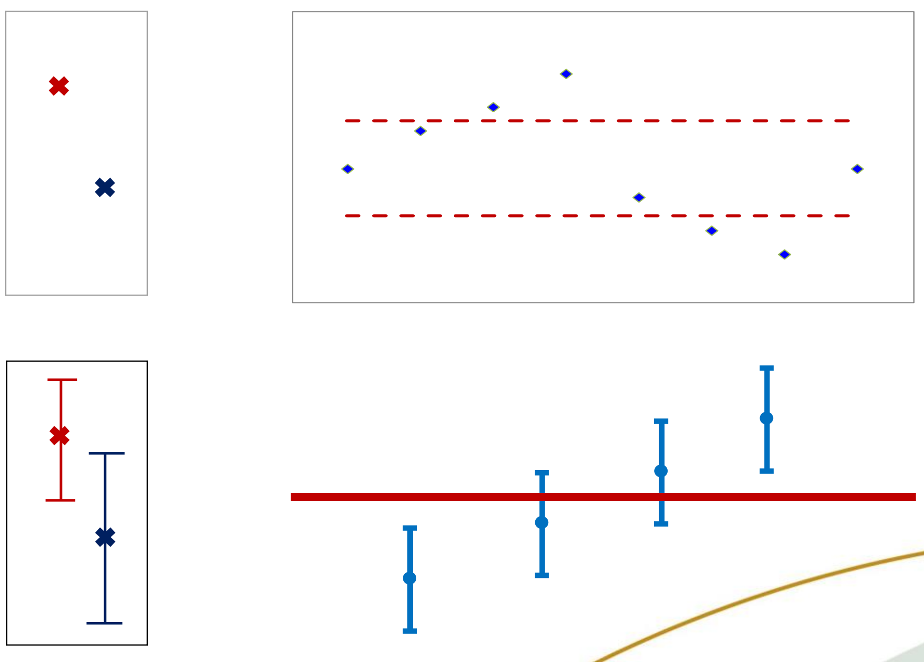
- Purity of Cu-metal: Certificate of Analysis from accredited RM producer (ISO 17034)
- Volume: Calibration certificate (ISO 17025 calibration laboratory)
  - Volume uncertainty one of the major contributions to final uncertainty
  - Glassware are likely to deform over time, so routine checking is recommended



- Temperature: Monitor temperature with thermometer or logger with smaller uncertainty then temperature control limits
  - Temperature specification = 20 ± 4 °C

Step 6: Uncertainty of Measurement

- Part of the definition of Traceability
  - "..each contributing to the measurement uncertainty"
- "spread of values that could reasonably be attributed to the measurand"



Step 7: Reporting traceability

- Calibration certificate
  - ISO 17025 requirement:
    - Specify chemical calibration standards used
    - Identity of measurement standards used to control measurement conditions (if significant)
- Test reports
  - Not required, but good practice to also identify calibration and measurement standards used

Conclusion

- Metrological Traceability – basis for establishing comparability of measurement results
  - Calibrated equipment, e.g. mass balance
  - Certified calibration standards
  - Validated methods
- Also assumed:
  - Qualified, trained staff
  - Equipment maintained
  - Reagent quality
  - Documented measurement procedures
  - Quality control

Metrological Traceability

SI

LAB A **LAB B**

Equ ent ?

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Thank You

We measure what matters

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