EURACHEM/CITAC Guidance on Metrological Traceability

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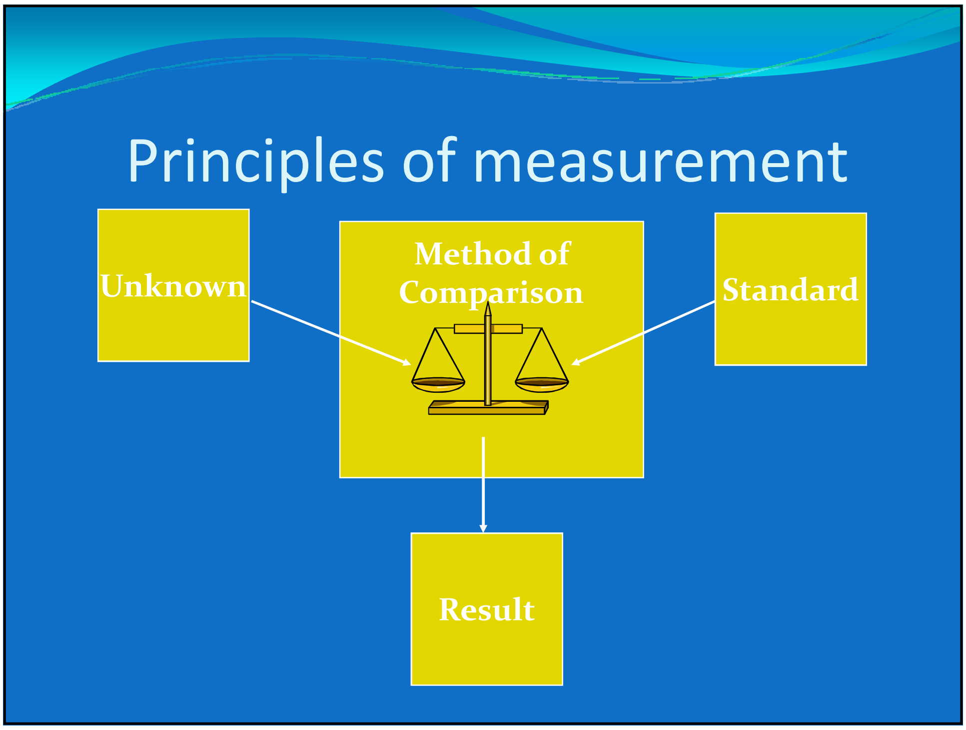
Traceability is easy

All results are traceable

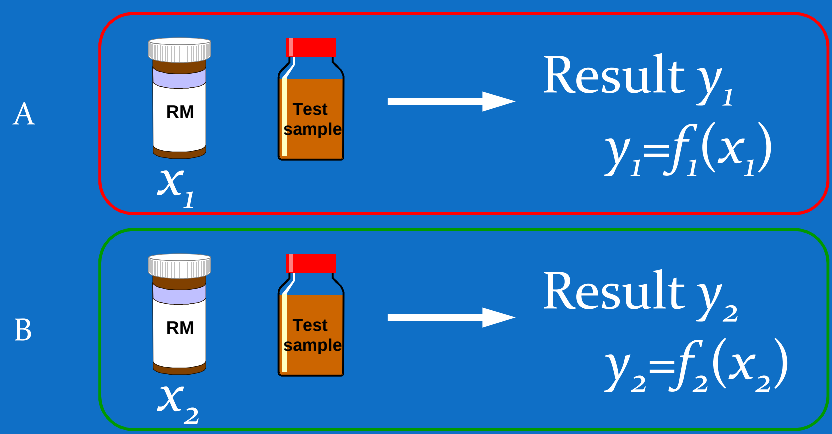
To what is the issue!


Principles of measurement
Unknown
Method of Comparison
Standard
Result

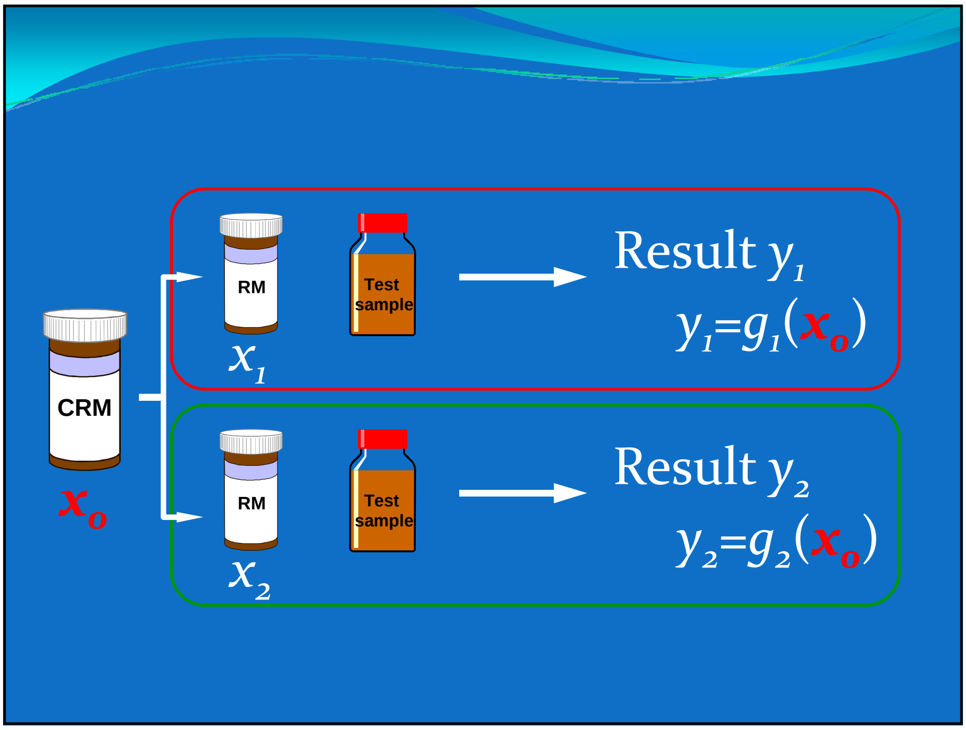

Let me show you!

Obtaining a traceable measurement

- Value of the result for an unknown is obtained from a comparison with the value of a calibration standard
  - e.g. measurement of mass
- Uncertainty of the result is the uncertainty of this comparison plus the uncertainty of the standard
- Value of the result is traceable to the value of the calibration standard
  - provided the method used for the comparison is valid and its uncertainty is known
- The value of the standard used must be traceable to agreed (international) standards
  - allows results to be comparable across space and time



Relationship between y_1 and y_2?



Validated Method

Traceability established for each parameter in the method

By calibration with appropriate standards.

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

- **The sole requirement for y to be fully traceable* is that $x_1 \ldots x_n$ are traceable or defined values**
- **Calibration of $x_1 \ldots x_n$ with appropriate standards is sufficient**

**other than MU requirements*

What is an appropriate standard?

Suitable unit preferably SI

Suitable uncertainty

Degree of control - 3 categories

- Green category: very small effect on the uncertainty minimal degree of control required,

Normal, routine laboratory equipment, reagents, etc able to provide appropriate references.

volume (beaker/measuring cylinder), time (wall clock), length (ruler), concentration (approx. 6 mol L^{-1} HCl), temperature (room temperature)

Amber Category: significant effect on the uncertainty,significant degree of control.

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Provided by appropriately maintained and calibrated equipment for common measurements (mass, volume, instrument response, etc). QA system of a properly equipped and appointed laboratory should provide appropriate references.

volumetric flask, analytical balance, common chemical reagents of specified concentration/purity (conc. nitric acid, acetonitrile HPLC grade)

Red category: also a significant degree of control, but analyst required to select the 'special' references needed to carry out a particular SOP.

materials with specified values (concentration/purity) used for instrument calibration, matrix reference materials used for QC, physical properties (molecular masses), individually calibrated glassware

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**other than MU requirements*

Example

Meeting the traceability requirements of ISO 17025: An analyst's guide (third edition)

http://www.nmschembio.org.uk

Determination of potassium iodide in vitamin tablets

Outline of Method

Weigh the ground sample into a crucible
Add ≈7 g potassium carbonate, mix, cover with further ≈10 g
Place in a muffle furnace at 675 C to 700 C for 25 minutes
Cool, add ≈ 20 mL of water, heat to boiling, filter into a flask
Make the volume to ≈ 200 mL
Add 7 mL bromine water to convert to potassium iodate
Add 2 mL phosphoric acid to remove excess bromine
Add 5 mL 16% w/v KI solution to yield iodine
Titrate with 0.01 mol L^{-1} sodium thiosulfate

Write down and understand the equation used to calculate the analytical result

$$KI(\mu g/tablet) = \frac{(T\text{-}B) \times A \times M \times MW_{KI} \times 10^6}{6 \times 1000 \times W}$$

T	Titre (mL)
B	Blank titre (mL)
A	Mean weight of one tablet (g) (mean of 20 tablets)
MW_{KI}	Relative molecular mass of KI
W	Weight of sample used (g)
M	Molarity of sodium thiosulfate determined by standardisation against potassium iodate ($mol\ L^{-1}$):

$$M\ (mol\ L^{-1}) = \frac{\text{mass of } KIO_3 \times \text{Purity of } KIO_3 \times 1000 \times 6}{MW_{KIO_3} \times \text{volume of } Na_2S_2O_3}$$

MW_{KIO_3} Relative molecular mass of KIO_3

Obtain suitable traceable references for each of these.

Target uncertainty is 4 %
Therefore uncertainty on each these references < 1 %

Start with the very simple but necessary ones
These should be provided by laboratory QA system

Titre

Approximately 10 mL volume

Readily provided by class A burette with 0.05 mL graduations

Mass

Mass of 1 tablet approximately 1 g
4-figure analytical balance

Molecular masses

Obtainable from up-to-date tables with an uncertainty of < 0.1%

Molarity of the sodium thiosulphate

Commercially produced volumetric standard solution.
For example, a 0.1 mo1.1:^{1} sodium thiosulphate solution, with a tolerance factor of ±0.001 mo1.1:^{1}(i.e. ±1%) readily available.

Alternatively, the molarity of the sodium thiosulphate solution could be established experimentally by standardisation against potassium iodate.
Analytical grade potassium iodate -> 99.9% purity more than adequate .

In certain critical applications (e.g. where an analysis may be part of a legal dispute), the use of a CRM might be preferable, since there is less scope for criticism of a result .

Required degree of control for values in equation

T sample titre (mL) B blank titre (mL)	} volumetric glassware
A mean weight of one tablet (g) W weight of sample used (g)	} analytical balance
MW_{KIO_3} relative molecular mass of KIO_3 MW_{KI} relative molecular mass of KI	} calculated from tables
M molarity $Na_2S_2O_3$	standardised using KIO_3
mass of KIO_3 (g)	analytical balance
purity of KIO_3	reagent with required purity & uncertainty
volume of sodium thiosulphate (mL)	volumetric glassware

All values in equations are in either the amber or red category

Required degree of control for equipment

- Fused silica crucibles, 50 mL capacity, 57 mm diameter
- Filter papers, Whatman No. 541, 18.5 mm diameter
- Oven temperature

Summary (1)

- Write down the equations used to calculate the analytical result
- Identify any 'reagents' or equipment with specified values
- Identify the fixed conditions used in the method
- Obtain appropriate 'stated references' to which the above values may be related or traced
- An appropriate reference has a stated value in the required unit with acceptable uncertainty

Summary (2)

- Traceability to appropriate 'stated references' provides the uncertianty' that is required when the SOP is carried out
- The required uncertianty is that which is fit for purpose
  - the smallest possible uncertainty is not always necessary and consequently the highest level stated reference is not always necessary

More details and Examples

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