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 \rightarrow Method of Comparison \rightarrow Standard \rightarrow 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

\[
\begin{align*}
\text{Result } y_1 &= f_1(x_1) \\
\text{Result } y_2 &= f_2(x_2)
\end{align*}
\]

Relationship between \( y_1 \) and \( y_2 \)?
Validated Method

Traceability established for each parameter in the method

By calibration with appropriate standards.
\[ y = f(x_1, x_2 \ldots x_m) \mid x_{m+p}, x_{m+2} \ldots x_n \]

- 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.
  
  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.

\[ y = f(x_1, x_2, \ldots, x_m) \mid x_{m+1}, x_{m+2}, \ldots, x_n \]

- 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
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

\[
\text{KI (µg/tablet)} = \frac{(T-B) \times A \times M \times \text{MW}_{\text{KI}} \times 10^6}{6 \times 1000 \times W}
\]

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

\[
M = \frac{\text{mass of KIO}_3 \times \text{Purity of KIO}_3 \times 1000 \times 6}{\text{MW}_{\text{KIO}_3} \times \text{volume of Na}_2\text{S}_2\text{O}_3}
\]

\(\text{MW}_{\text{KIO}_3}\): 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 mol dm⁻³ sodium thiosulphate solution, with a tolerance factor of ±0.001 mol dm⁻³ (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)
- A: mean weight of one tablet (g)
- W: weight of sample used (g)
- MIO₃⁻: relative molecular mass of KIO₃
- MW₂S₄O₇: relative molecular mass of K₂S₂O₇
- M: molarity of K₂S₂O₇
- w: mass of KIO₃ (g)
- purity of KIO₃
- volume of sodium thiosulphate (mL)

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 uncertainty’ that is required when the SOP is carried out.
- The required uncertainty 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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