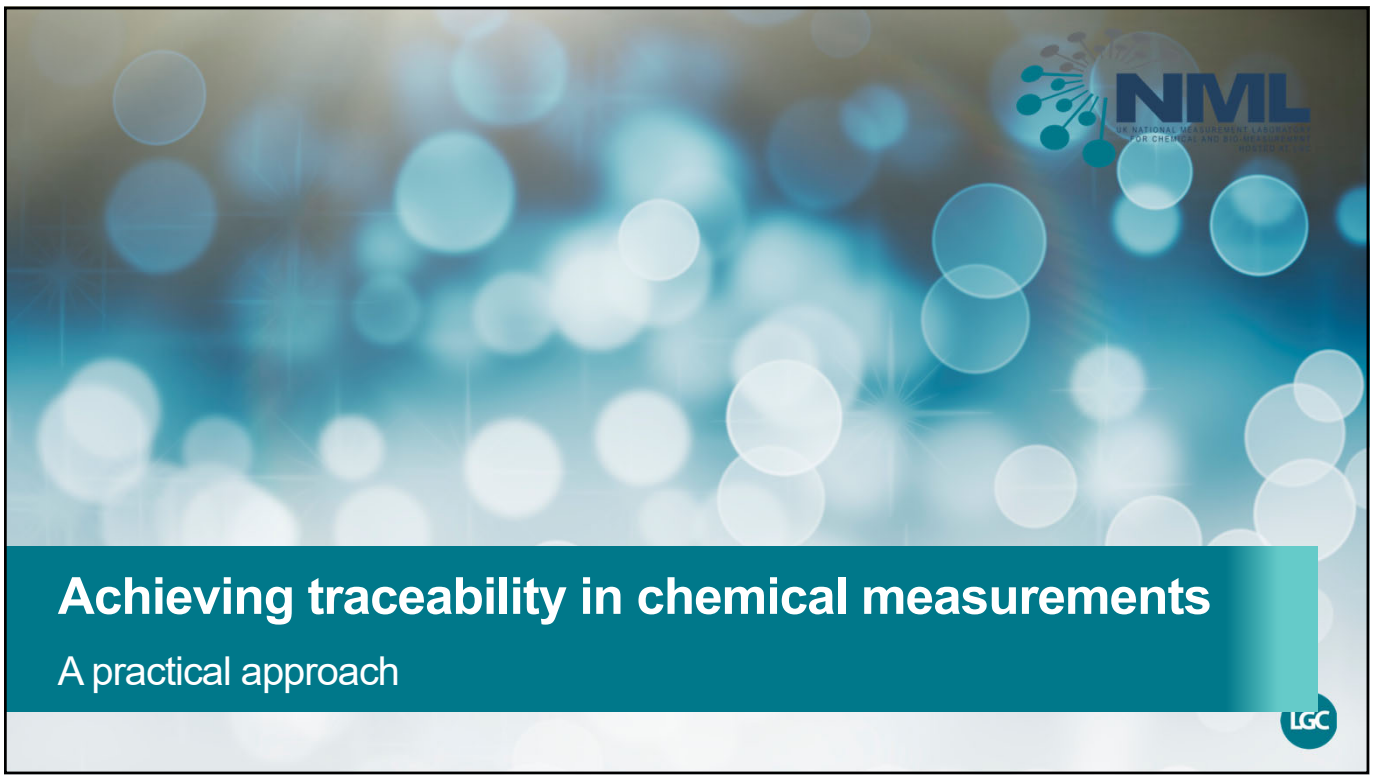

Overview

NML
UK NATIONAL MEASUREMENT LABORATORY FOR CHEMICAL AND BIO-MEASUREMENT HOSTED AT LGC

- Metrological traceability – a reminder
- Principles and the Eurachem guide
- Metrological traceability in practice
  - Key steps in attaining traceability
  - Stated references
  - Selecting appropriate stated references
- Worked example

LGC

Metrological traceability - reminder

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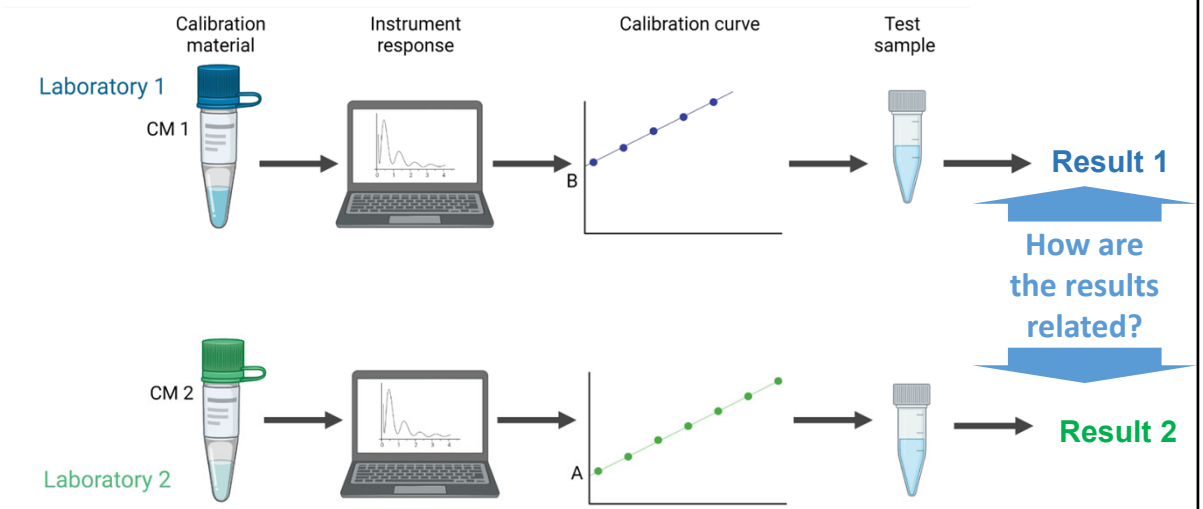
Why we need traceability



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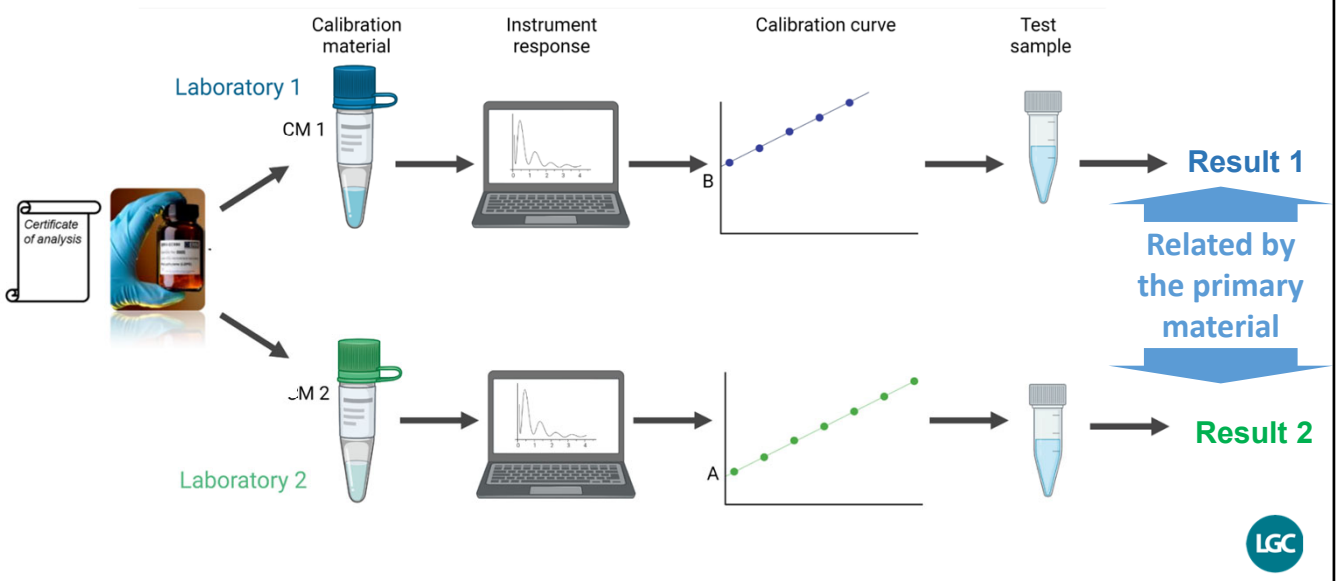
Why we need traceability



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Metrological traceability – definition

2.41 (6.10)
metrological traceability
property of a **measurement result** whereby the result can be related to a reference through a documented unbroken chain of **calibrations**, each contributing to the **measurement uncertainty**

References

- Definition of a measurement unit
- Measurement procedure including the measurement unit
- Measurement standard

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Establishing traceability - principles

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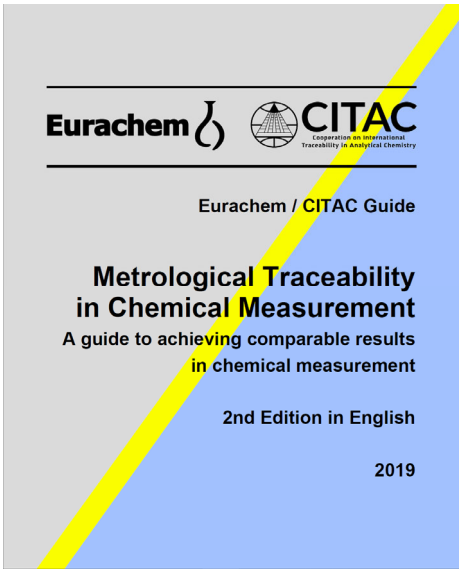
Metrological Traceability:

Principles of the Eurachem Guide

www.eurachem.org/guides



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The Guiding Principle

A measurement result arises from an equation

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

which is assumed to hold

under certain conditions

y is traceable to $x_1 \ldots x_n$

Implications: 1

If

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

- The sole* requirement for y to be traceable to higher references is that $x_1 \ldots x_n$ are traceable to higher references or are defined constants
- Calibration or control for $x_1 \ldots x_n$ is sufficient

**other than MU requirements*

Implications: 2

2. If we assume completeness for

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

- **The assumption(s) involved must be tested and shown to hold**

This is an essential part of method validation

Validation is crucial to practical traceability

Further implications

- Measurement uncertainty need only consider $x_1 \ldots x_n$
  - Nothing else affects the result y
- Validation and QC materials/references are not in the equation or specified conditions
  - No need to consider them part of the 'traceability chain'
- A result is traceable to/via *all of its input and control values*

  ∴ Cannot usually expect a simple statement of traceability to a single reference standard.

Establishing traceability - practice

Key steps in the attainment of traceability

- Write down and understand the equation 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’

Values appearing in the equation or specified in reagents, equipment or fixed conditions must be traceable to appropriate ‘stated references’

To achieve traceability

- The method must be properly validated and applied within its stated scope
  - if not, erroneous results may still be produced, even if all measurements and standards are traceable
- The method must be carried out using the appropriate stated references
  - how does the analyst select appropriate stated references?

What are ‘appropriate stated references’?

- Stated References
  - any ‘reference point’ that an analyst uses to obtain or realise a particular quantity or value in practice
- Physical calibrations are well established
  - calibrated weight; thermometer; volumetric glassware; stopwatch
- Chemical calibrations can be established in the same way
  - pure or matrix certified reference standards (calibrants); well-characterised pure materials

What is appropriate?

- The analyst must decide
- Depends on the degree of control that is required in obtaining or realising a particular value in practice
  - how much the quantity affects the result
- Uncertainty of each stated reference must be appropriate

Degree of control - Examples

- Instrument calibration standard
  - p,p'-DDE commercial grade chemical: purity >95%
  - p,p'-DDE certified reference material: certified purity 99.6±0.4%
- Sample preparation
  - weigh accurately 10±1 g of the solid, add about 50 mL of water, shake for 60 minutes, filter and make the volume to exactly 100 mL

Choosing the appropriate degree of control

- Fitness-for-purpose
  - acceptable uncertainty in final result: ±1%, ±5%, ±10%, ±50%?
- Method validation data
  - information on the effect of variations in fixed conditions
    - time, temperature
    - extraction/digestion reagents
    - clean-up procedures
- Analyst's experience

Degree of control - 3 categories

- Green category: a minimal degree of control in which normal, routine laboratory equipment, reagents, etc are able to provide appropriate stated references.
- Amber Category: a significant degree of control, such as that provided by appropriately maintained and calibrated equipment for common measurements such as mass, volume, instrument response, etc. The QA system of a properly equipped and appointed laboratory will normally provide the appropriate stated references.
- Red category: also a significant degree of control, but one which requires the analyst to select the 'special' stated references needed to carry out a particular SOP.

Examples

- Green - approximate measurements/specifications
  - volume (beaker/measuring cylinder), time (wall clock), length (ruler), concentration (approx. 6 mol L^{-1} HCl), temperature (room temperature)
- Amber - properly maintained and calibrated equipment
  - volumetric flask, analytical balance, common chemical reagents of specified concentration/purity (conc. nitric acid, acetonitrile HPLC grade)
- Red - special stated references needed
  - materials with specified values (concentration/purity) used for instrument calibration, matrix reference materials used for QC, physical properties (molecular masses), individually calibrated glassware

Establishing traceability - Example

Example: Determination of potassium iodide in vitamin tablets

- Outline of Method
  - Weigh (to four d.p.) the ground sample into a crucible
  - Overlay with ≈7 g potassium carbonate, followed by a 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, decant through a filter into a flask
  - Make the volume to ≈ 200 mL
  - Add 7 mL bromine water
  - Add 2 mL phosphoric acid and 5 mL 16% w/v KI solution
  - Titrate with 0.01 mol L^{-1} sodium thiosulphate
  - Standardise the sodium thiosulphate using potassium iodate

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

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

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

Write down the equation (continued)

- Molarity of sodium thiosulphate

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

MW_{KIO_3} Relative molecular mass of KIO_3

Required degree of control for values in equation

T	sample titre (mL)	volumetric glassware
B	blank titre (mL)	volumetric glassware
A	mean weight of one tablet (g)	analytical balance
W	weight of sample used (g)	analytical balance
MW_{KIO_3}	relative molecular mass of KIO_3	calculated from tables
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

2) Identify equipment/reagents with specified values

- Apparatus (section 3 of SOP)
  - 3.1 Fused silica crucibles, 50 mL capacity, 57 mm diameter
  - 3.2 Filter papers, Whatman No. 541, 18.5 cm diameter
- Reagents (section 4 of SOP)
  - 4.1 Purified water
  - 4.2 Phenol 80% w/w, reagent grade
  - 4.2.1 Phenol solution, 5% v/v
    Dilute 5 ml to 88 mL in a measuring cylinder
  - 4.8 Potassium iodate, analytical reagent grade
  - 4.9 Sodium thiosulphate, 0.1 mol L^{-1}

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Required degree of control for equipment/reagents

- 3.1 Fused silica crucibles, 50 mL capacity, 57 mm diameter
- 3.2 Filter papers, Whatman No. 541, 18.5 mm diameter
- 4.1 Purified water
- 4.2 Phenol 80% w/w, reagent grade
- 4.2.1 Phenol solution, 5% v/v
  - Dilute 5 mL to 88 mL in a measuring cylinder
- 4.8 Potassium iodate
  - AR grade: >99.9% CRM: 99.95 ± 0.05%
- 4.9 Sodium thiosulphate, 0.1 mol L^{-1}

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3) Identify fixed conditions (section 6 of the SOP)

- 6.1 Place in muffle set at 675 °C, for 25 minutes
- 6.4 Cool, add 20 mL of water
- 6.6 Add 7 mL bromine water, …boil, maintain volume of at least 200 mL
- 6.9 Add 2 mL phosphoric acid, 5 mL KI solution and titrate immediately with 0.01 mol L^{-1} thiosulphate solution

Required degree of control for fixed conditions

- 6.1 Place in muffle set at 675 °C, for approximately 25 minutes
- 6.4 Cool, add 20 mL of water
- 6.6 Add 7 mL bromine water, …boil, maintain volume of at least 200 mL
- 6.9 Add 2 mL phosphoric acid, 5 mL KI solution and titrate immediately with 0.01 mol L^{-1} thiosulphate solution

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
- Stated reference means any ‘reference point’ that an analyst decides to use

Summary (2)

- Traceability to appropriate ‘stated references’ provides the particular ‘degree of control’ that is required when an SOP is carried out
- The required ‘degree of control’ is that which is fit for purpose
  - the highest possible degree of control is not always necessary and consequently the highest level stated reference is not always necessary
- The analyst must choose the required degree of control, based on method validation data, intended end-use of the result, experience, etc.