ISO Fd Food ERA Chair
Safety
Quality
Traceability

"Quality assurance for Hg measurements in food and environmental samples"

25th - 27th November 2015

Traceability

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Materials:
http://tera.chem.ut.ee/~ivo/Temp/QA_Hg_Ljubljana_2015/

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The quality of the result of a chemical measurement

- **Validated measurement procedures**
- **Evaluated uncertainties of the results**
- **The results are traceable (to recognized reference points, i.e. measurement standards)**

- Demonstration of measurement proficicency by inter-laboratory comparison

On traceability:

Traceability in Chemical Measurement. Eurachem/CITAC, 2003. (available free of charge: http://www.eurachem.org/)

Traceability

- Traceability is a 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** 1 2 3 4

- Such a chain is called a **traceability chain**

JCGM 200:2012 International vocabulary of metrology — Basic and general concepts and associated terms (VIM 3)

Terminology

1

- Traceability **is** a property of
  - a measurement result or
  - a standard value or
  - a reference material reference value

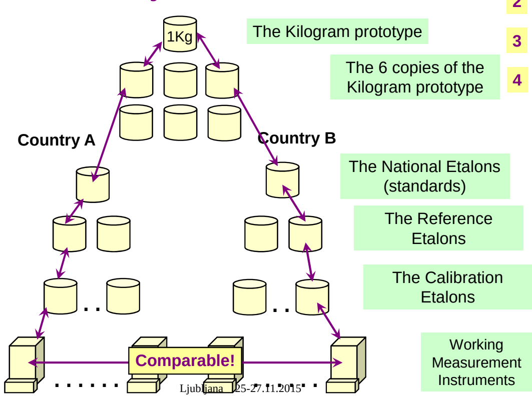
- Traceability **is not** a property of
  - a measurement or
  - a measurement procedure or
  - an institution

"Values are traceable to values!"

Traceability in physical measurements

- The (practical) **point of origin** (source) of a chain of traceability for a physical quantity is an international standard
- In the case of mass also the global point of origin is a physical object
  - Most other units are defined via fundamental constants
- The links of the chain are measurements (comparisons)
- Evaluation of uncertainty in physical measurements is well established

Traceability in mass measurement



Traceability chain

3

- The chain is in this case composed of calibrations
  - **Calibration** is an operation that, under specified conditions, in a

    first step, establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a

    second step, uses this information to establish a relation for obtaining a measurement result from an indication

How does this link with the usual calibration graphs used in analytical chemistry?

Traceability and comparability

3

- **The whole idea of establishing traceability is comparability of measurement results!**
- The results of two measurements are comparable only if they are:
  - expressed in the **same units**
  - traceable to the **same reference value that provides the same size of a unit in which the results are expressed**

Choice of references

2

- It is currently recommended to use, whenever possible, SI units as references
- This is called **traceability to the SI unit**
  - One SI unit (kg) is realized via a prototype
  - The others are realized via fundamental constants
- Using an SI unit is not always possible:
  - the octane value of gasoline
  - hardness according to Mohs' scale

Traceability of chemical measurement results

An excellent paper: B. King *Accred. Qual. Assur.* (2000), 5: 429-436

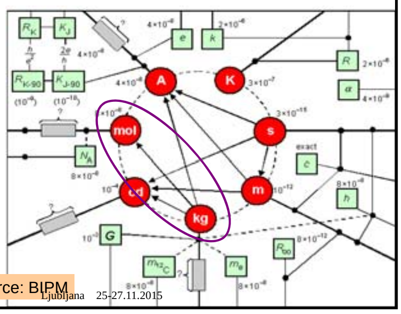
Amount of substance measurement

- Chemical measurements are as a rule **measurements of the amount of substance**
  - The substance is often called analyte
  - This **does not change** if the result is expressed in mg/l etc. instead of mol/l!
- **The analyte must be a defined entity**
  - The amount of every substance is essentially a different measurand
  - In amount of substance measurement it is of utmost importance that the **measured signal corresponds to the analyte** (and not to other substances!)
  - This is a **difference from all other SI units**

The Mole

The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12

- The mole is defined via the Kilogram



Source: BIPM

The Mole

- It is important to distinguish between two aspects:

- **Conceptual** (more important):
  - Mole as concept, related to the number of certain particles in certain object
  - **Atomic masses** that allow to relate the amounts of different substances to each other
    - This is how **weighing** obtains crucial importance in chemistry

- **Measurement unit** (less important):
  - Mole as unit for reporting measurement results

Formal traceability of amount of substance

- Formally traceability of amount of substance measurement is usually achieved as follows:
  - Standard solution of the analyte is prepared by **weighing** a certain mass of pure analyte
  - Sample containing the analyte is prepared in such a way that as large as possible part of the analyte (**ideally all analyte**) is transferred to a solution
  - The analyte content of the two solutions is **compared** using an analytical technique (spectrophotometry, chromatograpy, …)
    - The technique must be **selective**!

Chemical measurements: problems

- Problems in **defining** the measurand
- **Limited selectivity** of procedures, problems with quantification
- Problems in separating the analyte from the sample (instability, volatility, adsorbtion, …)
- Problems in sampling (collecting samples) and ensuring the samples are representative
- Problems with uncertainty estimation

Many different moles

- The mole is not a universal unit of amount of substance, instead there are **many different moles**
- In determining a specific analyte we want to measure the amount of only that substance
- **Selectivity becomes the main issue!**

Chemical measurements: measurand

- It is quite common for chemical measurements to be **operationally defined**:

- A specific analyte:
  - DIN 55609, Pigments and fillers: determining water soluble sulfates, chlorides and nitrates
  - ISO 3856, Paints and varnishes: content of soluble metals
- A nonspecific analyte
  - Various "total" acidities and basicities
  - Dietary fibre content of food
  - Oil pollution of snow

Chemical measurements: comparability

- **The total content of lead in paint and and the lead content determined using ISO 3856 procedure are not directly comparable!**

- … because these are different measurands

Stated reference in chemical measurements

2

- What could be the point of origin for a traceability chain in a chemical measurement?
- The mole does not have a “standard”:
  - Hundreds of thousads of substances
  - Thousands of matrixes
- Conclusion: it is not possible to create a “real” point of origin for the chain as a certified matrix reference material (CMRM)

Stated reference in chemical measurements

2

- Instead the traceability of amount of substance is taken from **mass measurement** of pure substances
- The point of origin:

Atomic masses obtained according to the definition of the mole and **weighing data**

- But large problems remain in relating these pure substance masses to the masses of substances in real matrices

Separating the analyte from the sample

- A key quantity is the **recovery (*R*)**
  - Difficult to determine reliably
  - Difficult to estimate uncertainty

Representativeness of samples

- Often the most important source of the total uncertainty
- Usually analysts do not collect the samples themselves
- In this case the result should be supplied with clear references stating whether it relates to:
  - the laboratory sample or
  - the bulk material being analysed

Establishing traceability in chemical measurements

Establishing traceability

- We present the Eurachem/CITAC approach
- A practical approach
- Traceability is established in a stepwise process
- Only when all the stages have been completed can we claim that our measurement result is traceable to a reference value

Traceability in Chemical Measurement. Eurachem/CITAC, 2003. (available free of charge: http://www.eurachem.org/)

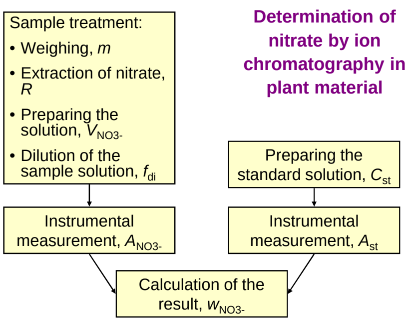
Establishing traceability: stages

1. Defining the measurand
2. Choosing a suitable procedure
   - Measurement procedure
   - Mathematical model
3. **Validation**: demonstrating that
   - The measurement model adequatly describes the measurement
   - The measurement conditions are adequate (Selectivity! Recovery/trueness!)
4. Establishing traceability for all input quantities (or groups of quantities)
   - Choosing standards and **reference materials**
   - Using them for **calibration**
5. Evaluating the **uncertainty** of the result

1. Defining the measurand

- Let us consider Nitrate determination by ion chromatography in plant material dried to constant weight under specified conditions
- The measurand is the **total nitrate content** in the dried plant material: w_{NO3^-} expressed in mg/g

2. Choice of procedure : measuring



2. Choice of procedure: mathematical model

$$w_{NO_3^-} = C_{st} \frac{A_{NO_3^-} \cdot V_{NO_3^-}}{A_{st} \cdot m} \times f_{di} \times \frac{1}{R}$$

w_{NO3^-}	*nitrate content of the sample (mg/g)*
C_{st}	*nitrate concentration in standard solution (mg/l)*
A_{NO3^-}	*intensity of the signal for sample solution (mS·s)*
A_{st}	*intensity of the signal for standard solution (mS·s)*
V_{NO3^-}	*volume of sample solution (l)*
m	*mass of the dried sample (g)*
f_{di}	*dilution factor (no units);*
R	*recovery factor (cf. sample preparation)h*

3. Validation

- **Analyte identity? Interferences?**
  - Any overlap of peaks?
  - Can we be sure that there are no interfering peaks where the analyte peak appears?
- **Model adequate?**
  - Does the procedure being used determine all of the nitrate present?
  - Has incomplete extraction of the analyte from the sample been accounted for?
- **Measurement conditions adequate?**
  - We are using one point calibration. Therefore we must find out:
    - Is the calibration plot linear?
    - Is the y-intercept close to zero?

4. Calibration

- Calibration must be performed by reference standards
  - with demonstrated traceability and
  - adequately small uncertainty
- Calibration involves standard solution
- Here atomic masses are involved:
  - Solution is prepared from KNO_3 (M = 101.11 g/mol)
  - The analyte is NO_3^- (M = 62.01 g/mol)

4. Establishing traceability for all input quantities

The means of establishing traceability:

Manufacturer's certificate

$$Q_{NO_3^-} = C_{st}\frac{A_{NO_3^-}}{A_{st}}\frac{V_{NO_3^-}}{m}\times f_{di}\times\frac{1}{R}$$

calibration (solution-RM or pure substance RM)

gravimetry

Matrix-CRM (determining R)

5. Evaluating the uncertainty of a result

- If traceability has been established for all the input quantities then we automatically have their uncertainties (definition of traceability!)
  - There can still be practical problems with *R*

Traceability established!

- **If all these stages have been successfully completed then we can claim our measurement result to be traceable to the unit in which it is expressed**

Thank you for your participation!

- The materials are available from:
  http://tera.chem.ut.ee/~ivo/Temp/QA_Hg_Ljubljana_2015/

- You are always welcome to contact me:
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