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 proficiency by inter-laboratory comparison

On traceability:

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
- 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

- 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

The Kilogram prototype
- The 6 copies of the Kilogram prototype

Country A
- The National Etalons (standards)
- The Reference Etalons
- The Calibration Etalons

Country B
- Working Measurement Instruments

Comparable!
Traceability chain

• 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

• 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

• 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


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

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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, chromatography, …)
    - 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, adsorption, …)
- 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 the lead content determined using ISO 3856 procedure are not directly comparable!
- … because these are different measurands
Stated reference in chemical measurements

• What could be the point of origin for a traceability chain in a chemical measurement?
• The mole does not have a “standard”:
  – Hundreds of thousands 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

• 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

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: $W_{NO_3^-}$ expressed in mg/g

2. Choice of procedure: measuring

Sample treatment:
- Weighing, $m$
- Extraction of nitrate, $R$
- Preparing the solution, $V_{NO_3^-}$
- Dilution of the sample solution, $f_{di}$

Preparation of the standard solution,

Instrumental measurement, $A_{NO_3^-}$

Calculation of the result, $W_{NO_3^-}$

Mathematical model

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

- $W_{NO_3^-}$: nitrate content of the sample (mg/g)
- $C_m$: nitrate concentration in standard solution (mg/l)
- $A_{NO_3^-}$: intensity of the signal for sample solution (mS·s)
- $A_{st}$: intensity of the signal for standard solution (mS·s)
- $V_{NO_3^-}$: volume of sample solution (l)
- $m$: mass of the dried sample (g)
- $f_{di}$: dilution factor (no units)
- $R$: recovery factor (cf. sample preparation)

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:
  - Calibration (solution-RM or pure substance RM)
  - Manufacturer’s certificate
  - Gravimetry
  - Matrix-CRM (determining R)

\[ Q_{NO_x} = C_{NO_x} \frac{V_{NO_x}}{A_y/m} \times f_A \times \frac{1}{R} \]

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: ivo.leito@ut.ee

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