Environmental Chemical Analysis – Analysis Quality

Graduation in Chemistry and Technological Chemistry

Environmental analysis quality

2025/26

Topic

Measurement Traceability
Rastreabilidade da Medição (PT)

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http://mechem.rd.ciencias.ulisboa.pt/

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Principles: Measurement uncertainty concept

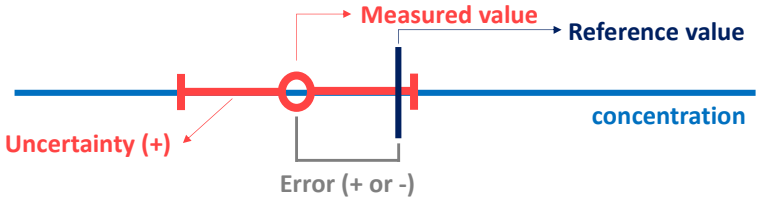
- **Definitions**

Measurand: “quantity intended to be measured”

Error: “measured quantity value minus a reference quantity value”

Uncertainty: “non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used”

Measurement result:



JCGM, International vocabulary of metrology — Basic and general concepts and associated terms (VIM), JCGM 200, 2008. (http://www.bipm.org).

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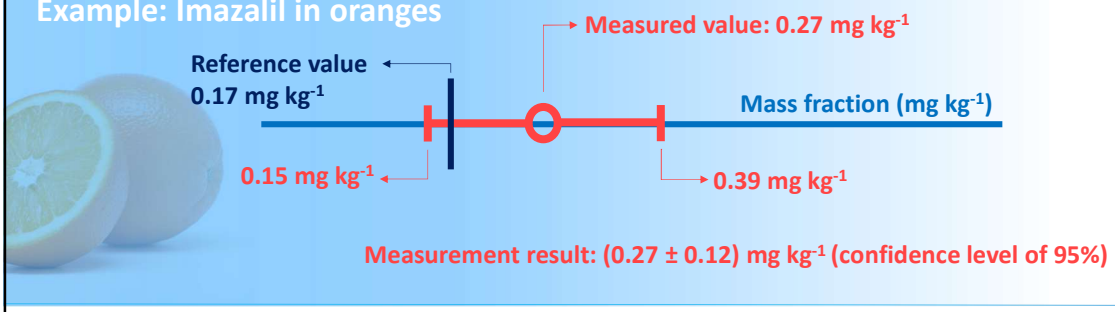
Principles: Measurement uncertainty concept

Uncertainty: "non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used"

Example: Imazalil in oranges



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Principles: Measurement uncertainty concept

Uncertainty: "non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used"

Measurements reported without uncertainty are only interpretable by the analyst responsible for the analysis.

Measurements reported with uncertainty can be interpreted by everyone.

[this feature is essential to regulate the international market]

Principles: Measurement uncertainty concept

Uncertainty: "non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used"

The measurand is defined considering the:

- » Analysed item
- » Analysed parameter
- » Target measurement traceability (if relevant)

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Principles: Measurement uncertainty concept

Uncertainty: "non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used"

Examples of analysed item:

Determination of lead in kaolinitic clay

(clay mineral used as feed additive for calf with the chemical composition $Al_2Si_2O_5(OH)_4$)

2 tons of kaolinitic clay

1 kg of kaolinitic clay

IRMM, Determination of extractable and total lead in kaolinitic clay, JRC 69122, 2012.

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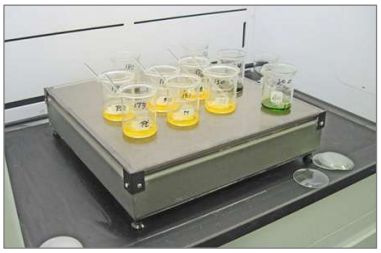
Uncertainty: "non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used"

Examples of parameters:

Determination of lead in kaolinitic clay

Total Pb



Acid extractable Pb
(5% HNO_3; boiling for 30 min)

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Principles: Measurement uncertainty concept

Uncertainty: "non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used"

Examples of parameters: Determination of lead in kaolinitic clay	Measurand definition
	Total Pb: Rational measurand
	» Total Pb in kaolinic clay sample S1234 (parameter) (item)
	Acid extractable Pb: Operationally defined measurand
	» Pb extractable with boiling 5% nitric acid in sample S1234 (parameter) (analytical method) (item)

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Rational measurands

Total Pb in a lettuce sample – Acid digestion of the sample (100 % efficiency) and analysis of the sample solution by atomic spectroscopy

Nitrate in water – Ion chromatographic analysis after sample dilution

pH in water – Potentiometric measurement of pH

Methane concentration in gas – Determination by chromatography equipped with a flame ionization detector (FID)

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Operationally measurands

Moisture content in soil – Defined as the amount of water in a food sample, measured using oven drying

Protein content in food – Defined as the amount of protein in a food sample, measured using the Kjeldahl method or Dumas combustion method (expressed as a percentage)

Sugar content in food (Brix Value) – Defined as the percentage of soluble solids (mainly sugars) in a food sample, measured using a refractometer (expressed in °Brix).

Acidity (Titratable Acidity) – Defined as the concentration of acidic compounds in a food sample, measured using acid-base titration (expressed as % acid content).

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Principles: Measurement uncertainty concept

Exercise:

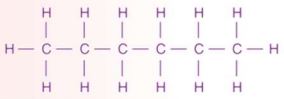
Which of these measurements are operationally defined or rational?

(1) Determination of suspended matter in wastewaters
(mass of matter from 1 L of water collected in a 1.5 µm pore filter after drying between 103 ºC and 105 ºC)

(2) Determination of total Cd in a soil sample ***(complete acid digestion of an analytical portion and subsequent analysis of a solutionof Cd by atomic spectroscopy)***

(3) Determination of nitrate in treated efuent
(determination of nitrate by ion chromatography after sample dilution)

(4) Determination of oil and grease in a wastewater ***(mass extracted with n-hexane determined after solvent evaporation)*.**



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Principles: Measurement traceability concept

- **Measurement traceability concept**

The measurement uncertainty concept is intimately related to the measurement traceability concept since the last one involves defining a reference for the measurement.

National traceability example:

Dry measures standards from D. Sebastião kingdom

Dry measures are units of volume used to measure bulk commodities which are not liquid. They were typically used in commodity markets to measure grain, dried beans, and dried and fresh fruit.

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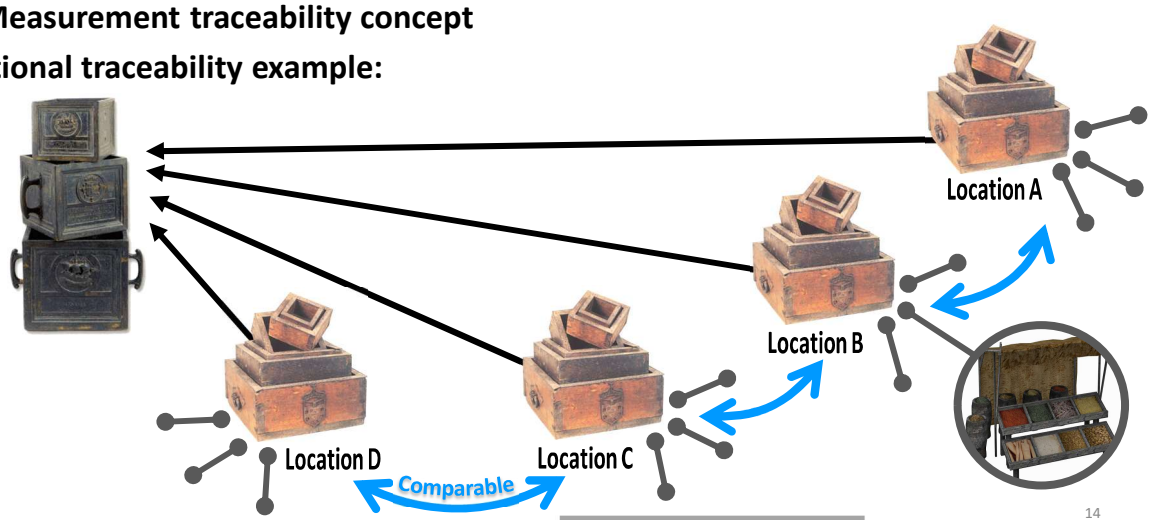
Principles: Measurement traceability concept

- **Measurement traceability concept**

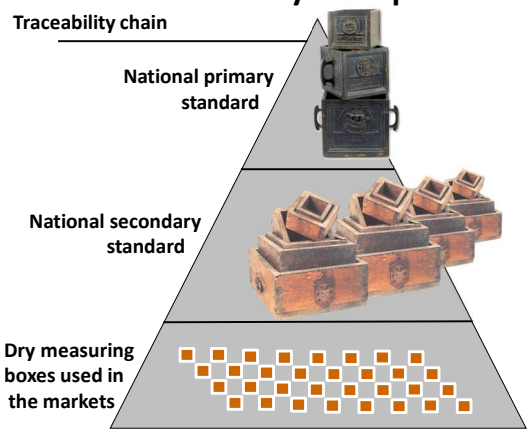
National traceability example:



Principles: Measurement traceability concept

- **Measurement traceability concept**

National traceability example:



Dry measures
(Tiles panel, Customs Lisbon)

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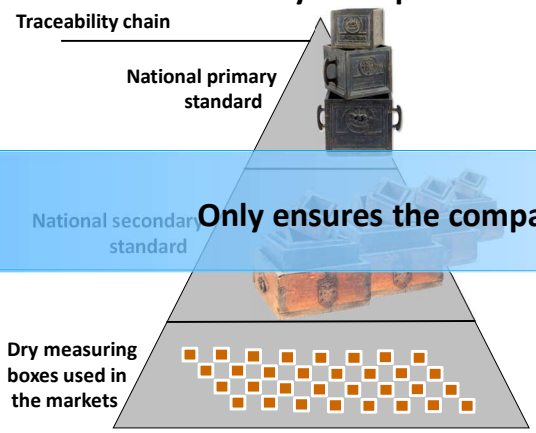
Principles: Measurement traceability concept

- Measurement traceability concept

National traceability example:



Only ensures the comparability of national measurements

Dry measures
(Tiles panel, Customs Lisbon)

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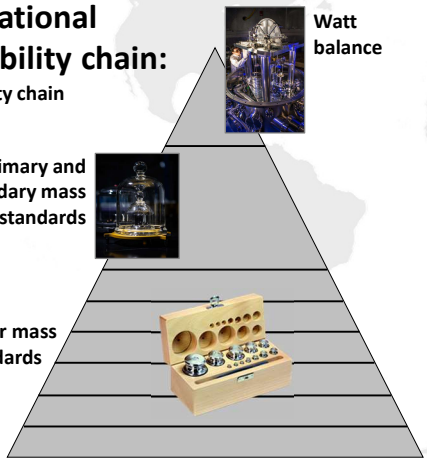
Principles: Measurement traceability concept

- **Measurement traceability concept**

International traceability chain:

Traceability chain

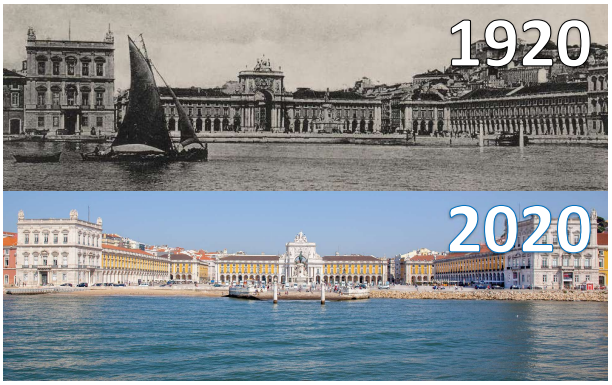


Traceability chains should be selected depending on how far comparisons need to be performed and how low measurement uncertainty should be.

Principles: Measurement traceability concept

- **Measurement traceability concept**

Need for low uncertainty



Need for temporal stable references

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Principles: Measurement traceability concept

VIM defines measurement traceability as:
"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".

All measurements are traceable to a reference. This reference can be local, national or international and supports the comparability of results traceable to it. Sometimes the used reference is unstable or is ambiguously defined. The main goal of assessing measurement traceability is to check if measurement reference is adequate.

JCGM, International vocabulary of metrology — Basic and general concepts and associated terms (VIM), JCGM 200, 2008. (http://www.bipm.org).

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Principles: Measurement traceability concept

Comparability: "comparability of measurement results, for quantities of a given kind, that are metrologically traceable to the same reference".

Quantity: "property of a phenomenon, body, or substance, where the property has a magnitude that can be expressed as a number and a reference".

Kind of quantity : "aspect common to mutually comparable quantities"

Example: The quantities diameter, circumference, and wavelength are generally considered to be quantities of the same kind, namely of the kind of quantity called length.

JCGM, International vocabulary of metrology — Basic and general concepts and associated terms (VIM), JCGM 200, 2008. (http://www.bipm.org).

Principles: Measurement traceability concept

Selection of the measurement reference:

1) Common reference to measurement results or values to be compared with

2) Reference capable of producing measurements with adequately low uncertainty

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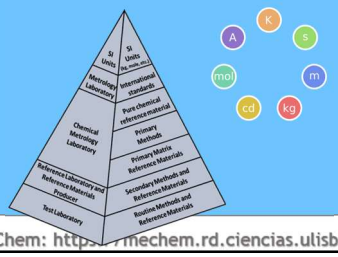
Principles: Measurement traceability concept

Types of traceability chains in measurements in chemistry

Traceability to specific SI units

(e.g. "mg L^{-1}", "mg kg^{-1}", "mol L^{-1}", "cg g^{-1}" and "cL L^{-1}")

Measuring system must be calibrated with materials with reference values traceable to the SI units.



Traceability to the value embodied in a reference material

(using SI units without metrological accuracy; e.g. organic compound purity estimated by GC-FID using total area method)

Traceability to the value defined by the measurement procedure

(i.e. applicable to empirical or operationally defined measurement procedures; e.g. determination Pb extractable in specific acid conditions).

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Principles: Measurement traceability concept

- **References:**

Measurement uncertainty principles:

JCGM, Evaluation of measurement data – Guide to the expression of uncertainty in measurement, JCGM 100, 2008. (www.bipm.org)

Eurachem/CITAC, Quantifying Uncertainty in Analytical Measurement, Third edition, 2012. (www.eurachem.org)

Measurement traceability:

Eurachem/CITAC Guide: Metrological Traceability in Analytical measurement, Second edition, 2019. (www.eurachem.org)

P. De Bièvre, R. Dybkaer, A. Fajgelj, D. B. Hibbert, Metrological traceability of measurement results in chemistry: Concepts and implementation, Pure Appl. Chem. 83 (2011) 1873–1935.

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Principles: Measurement traceability concept

Exercise:

Define the measurement traceability:

(1) Determination of oil and grease in a wastewater
***(mass extracted with n-hexane determined after solvent evaporation)*.**

(2) Mass fraction of total mercury in sediments

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Principles: Measurement traceability concept

Exercise:

Define the most relevant advantage of tracing measurements to an SI unit:

» Ensuring that two labs using the same standard get comparable results
» Ensure the use of the cheapest standards
» Ensure produced measurements can be comparable with the ones collected in the future
» To be committed to French Revolution achievements

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