

Comparability and Traceability

Point of view from a metrological institute

Ed W.B. de Leer

NMi Van Swinden Laboratory

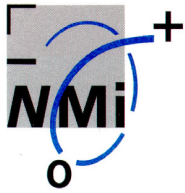
Delft, The Netherlands

My Discussions in Metrologyland



The CCQM in 1996

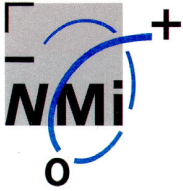




Traceability Definition

property of the result of a measurement or value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties

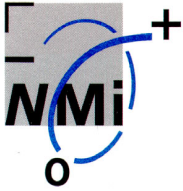
VIM 1993



Traceability Questions

property of the result of a measurement or value of a standard (?) whereby it can be related to stated references (??), usually national or international standards (????), through an unbroken chain of comparisons (????) all having stated uncertainties (?????)

VIM 1993



Result of a Measurement

Traceability is a property of the result of a measurement !

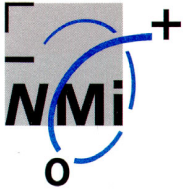
ISO/IEC 17025:1999 paragraph 5.6.2.1

... ensure that calibrations and measurements made by the laboratory are traceable to

ISO/FDIS 15189 (version 2000) par. 5.6.3

... ensure that measurements are traceable to

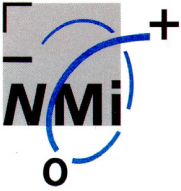
...



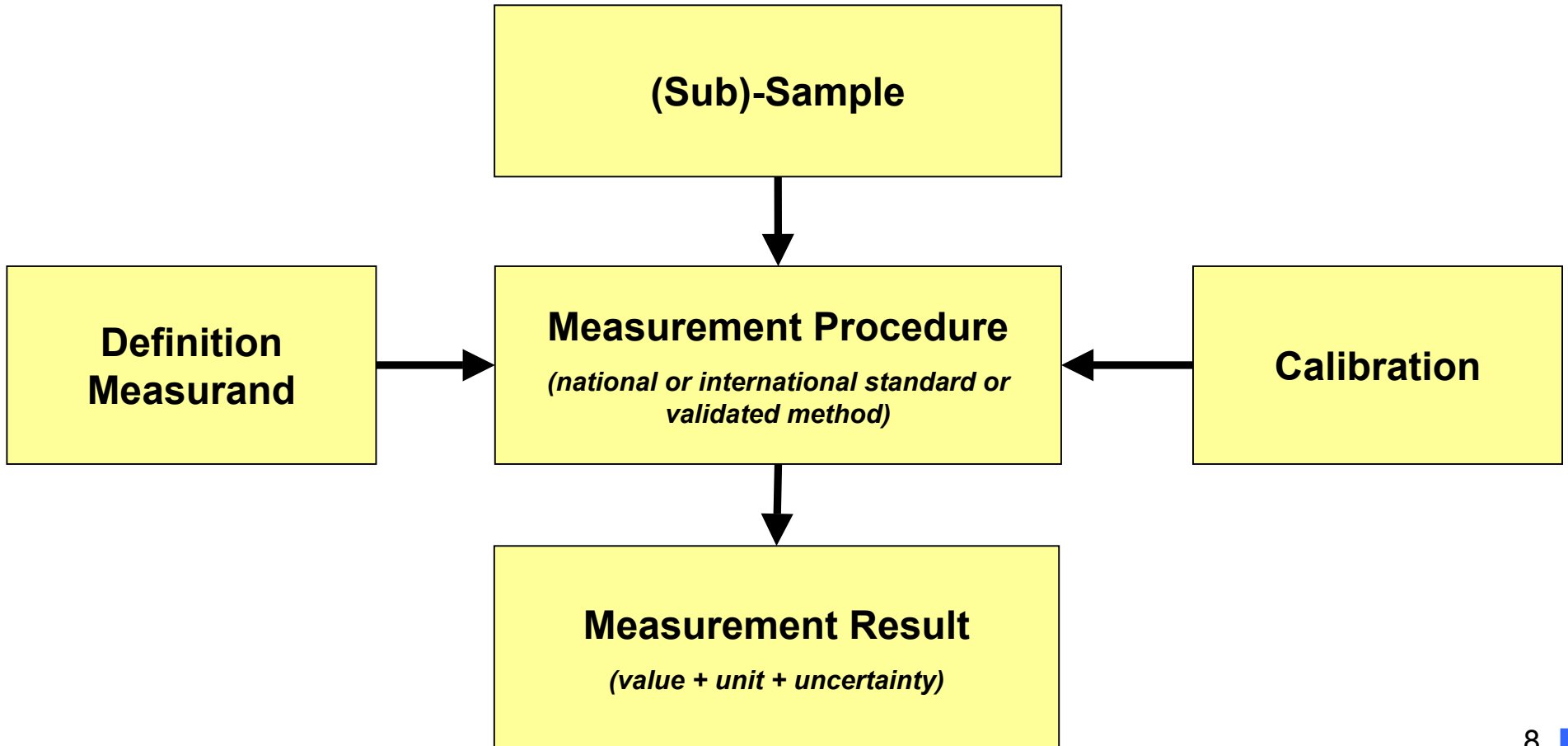
Stated References

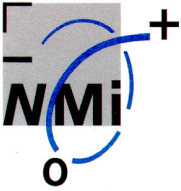
Traceability to:

- a reference material with arbitrarily assigned and (inter)nationally accepted values ?
- a certified reference material with consensus values ?
- a certified reference material with reference values assigned with “primary” methods ?
- a calibration standard ?
- a written standard (traceability to a method) ?

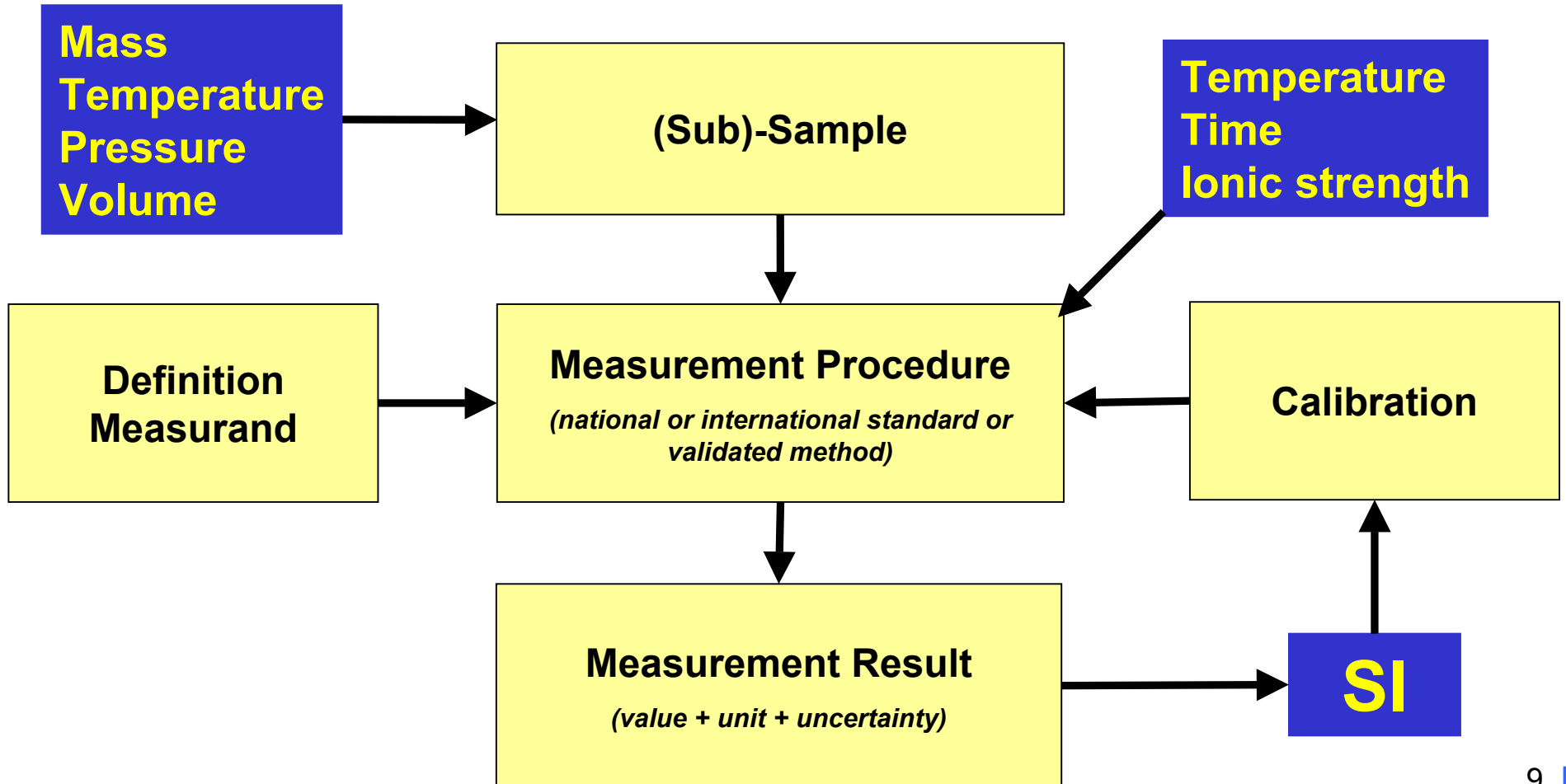


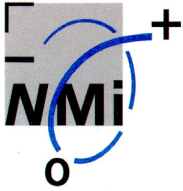
Measurement Process





Traceability to SI



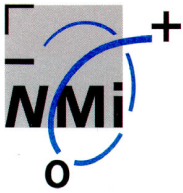


Definition of the Measurand

Proper definition of the measurand avoids the discussion about traceability to a method

- Mass fraction of benzo(a)pyrene in soil in mg/kg on a dry weight basis (= total BaP)
- Mass fraction of benzo(a)pyrene in soil in mg/kg on a dry weight basis after extraction according to ISO xxxx (~65%)
- Mass fraction of benzo(a)pyrene in soil in mg/kg on a dry weight basis after exhaustive Soxhlet extraction according to ISO yyyy (~95%)

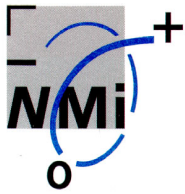
In many cases the object should be defined as well !



Traceability to a Reference Material

Reference materials are used mainly for:

- **calibration**
 - **validation of the measurement procedure**
 - **statistical quality control**
-
- **Calibration RMs are the first step in a traceability chain.**
 - **Validation RMs provide validation data and uncertainty information – no traceability**



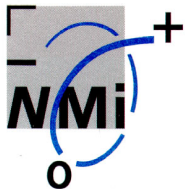
Value Assignment to RMs

Calibration reference materials

- **Gravimetry + validation**
- **Primary methods (e.g. coulometry, IDMS)**

Validation reference materials (traceable values required !)

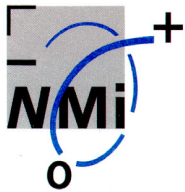
- **Primary methods**
- **Consensus for measurands that include a method in the definition**
- **Consensus from the application of different methods of assumed definitive character**
- **Consensus from different methods**



Traceability to a Reference Material

**Calibration
RMs with an
internationally
accepted
arbitrary value
(artefacts) may
as well provide
traceability**



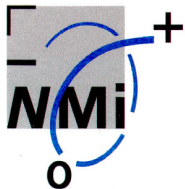


Measurement Uncertainty

Before 1995, analytical chemists interpreted “measurement uncertainty” mostly as some form of reproducibility. The GUM was (and still is) rather unknown

In 1995 the first edition of the “Eurachem Guide” was published. Second edition in 2000. More than 40.000 downloads

In 2001/2002, EA and ILAC policy with respect to the introduction of MU in testing was formulated (ISO/IEC 17025). ISO and CEN consider MU as a standard paragraph in new standards.



Primary Standard Substances

A.I. Vogel (1939)

A textbook of quantitative inorganic analysis

- 1. Easy to obtain, purify, dry and preserve**
- 2. Should be unaltered during weighing**
- 3. Total impurities should not exceed 0.01-0.02%**
- 4. Should have a high equivalence weight**
- 5. Should be readily soluble**
- 6. Reaction should be stoichiometric and practically instantaneous**

Primary Methods



Primary thermometry we define as thermometry carried out using a thermometer for which the equation of state can be written down explicitly without having to introduce unknown, temperature-dependent, constants.

$$PV_m = N_A kT$$

Read my book!

Primary Ratio Methods



Primary ratio thermometry was defined for those cases where the constants in the equation of state are unknown but independent of temperature

$$\frac{E'(T)}{E'(T_0)} = \frac{T^{-4}}{T_0^{-4}}$$

$$E'(T) = \varepsilon Ag \sigma T^{-4}$$

Primary Methods

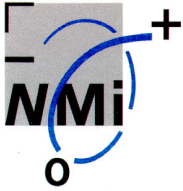


A primary method of measurement in the SI is a method having the highest metrological qualities whose model (mathematical equation) and realization are completely described and understood in terms of SI units

The use of a primary direct method results in a value of an unknown quantity without reference to a standard of the same quantity.

The use of a primary ratio method results in a value of the ratio of two values of the same quantity without reference to a standard of the same quantity.

In both cases, the results must be accompanied by a complete uncertainty statement



Potential Primary Methods

Gravimetric analysis

Volumetric analysis

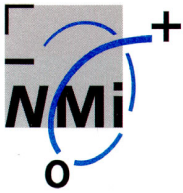
Coulometry

Isotope dilution mass spectrometry

Thermochemical techniques

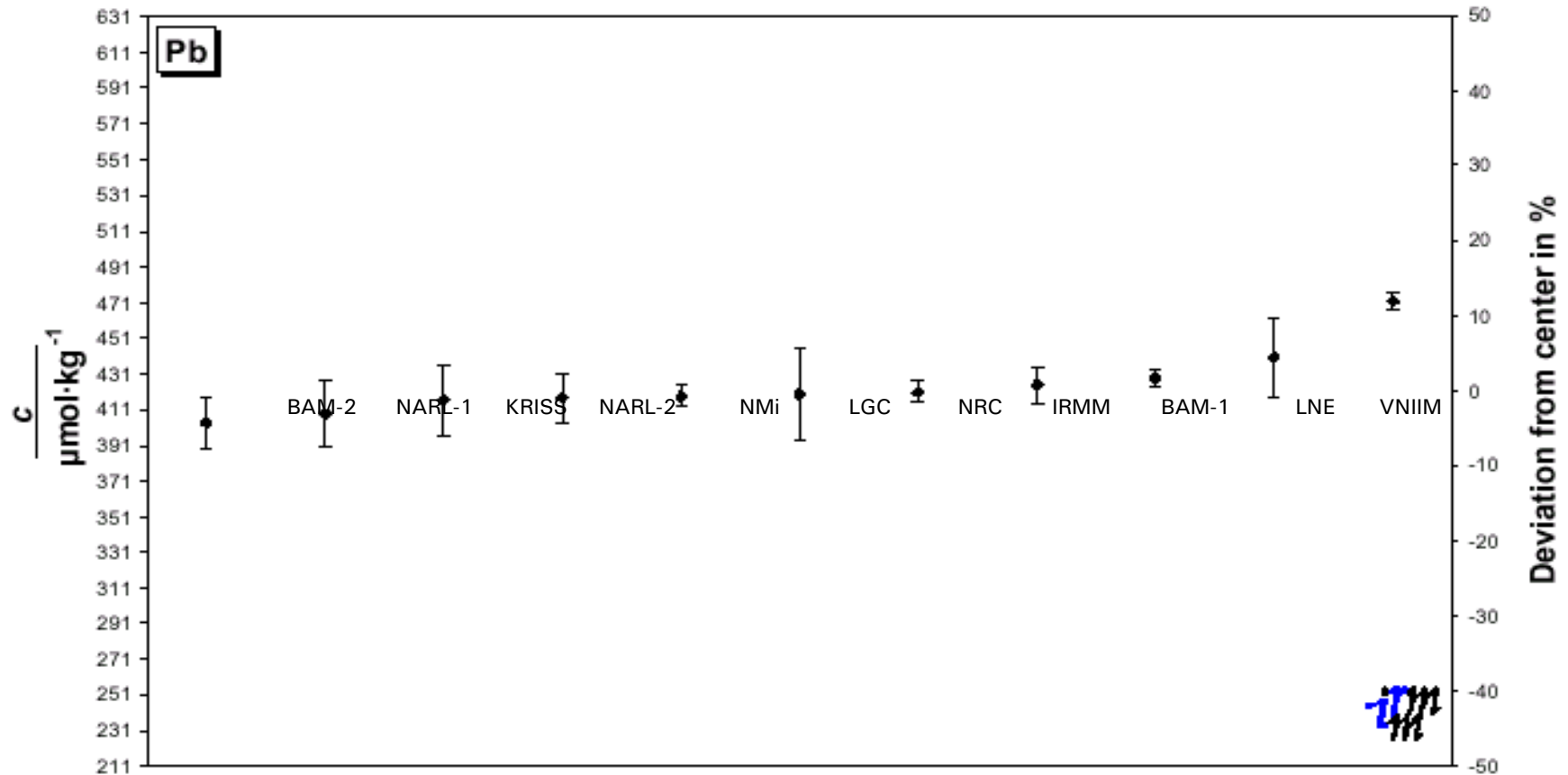
The major problem in chemical analysis is lack of specificity, which is not solved by primary methods

High accuracy methods could be better !



National Metrology Institutes

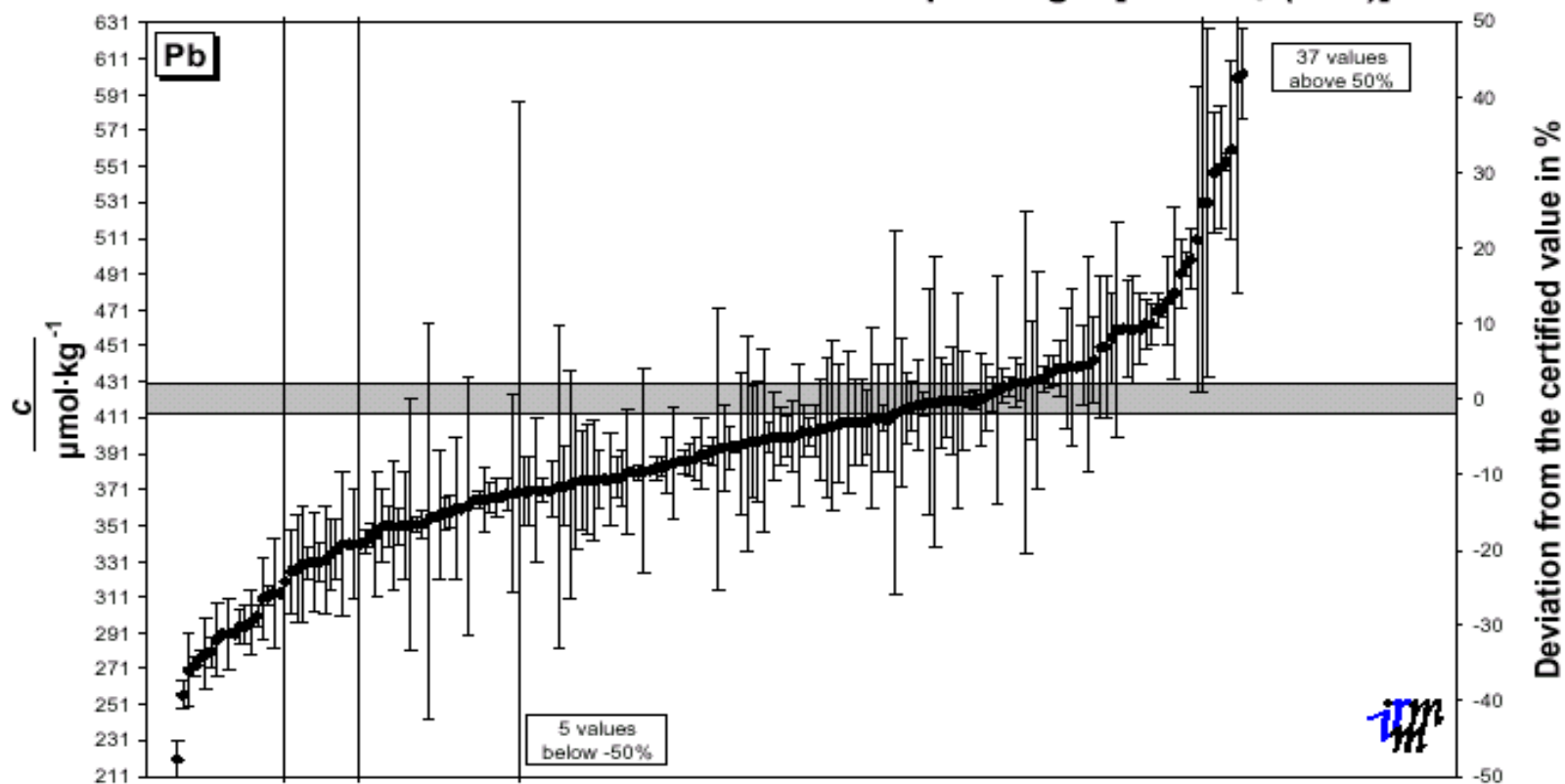
CCQM-P15 : Pb and Cd in sediment



Field Laboratories

IMEP- 14 : Trace elements in sediment

Certified value : $421.1 \pm 8.4 \mu\text{mol}\cdot\text{kg}^{-1}$ [$U=k \cdot u_c$ ($k=2$)]



Results from all participants.

The CCQM in 2001

