Principles and Purpose of Traceability

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Traceability:

Property of the

- result of a measurement or → **A posteriori**
- the value of a standard → **A priori**

whereby it can be related to

- stated references, usually national or international standards, through
- an unbroken chain of comparisons all having stated uncertainties

(current VIM Definition)

Two key components to traceability:

- standards $\pm u_{st}$

- uncertainty $\pm u_{pr}$

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combined uncertainty:

$$u_x = \sqrt{u_{st}^2 + u_{pr}^2}$$

Practical steps towards traceability

- Follow a clear procedure
- Identify and procure all standards/ references/étalons
- Guesstimate the influence of each on the measurement uncertainty
- Minimize the large contributions to uncertainty
- Optimize: Produce a smaller uncertainty and a better estimate

Environmental Methods: The central role of the procedure

- Total Phosphorus in Water
- Adsorbable Organic Halogens in Water (AOX)
- Chemical Oxygen Demand of Water (COD)
- Metals in Precipitated Particulate Matter from Atmosphere
- Dissolved Oxygen in Water

The Measurement of pH

IUPAC Working Party on pH

- Notational definition:

$$pH = -\lg a_H = -\lg\left[\frac{m_H \gamma_H}{m^0}\right]$$

- Operational definition:

$$Pt \mid H_2 \mid buffer\, S, Cl^- \mid AgCl \mid Ag$$

Operational Definition of pH

- Debye-Hückel formalism with Bates-Guggenheim convention
- (only) 5 primary buffers
- $3 < pH < 10$
- $I < 0.1$ mol/l
- Aqueous solution

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The nature of „stated references":

- Time
- Temperature
- Pressure
- Length:
  - Diameter
  - Volume
- Amount of substance: chemical standards
- ....

Two „types“ of stated references:

1. with *little* influence on final result
2. with *large* influence on final result

Ad 2)

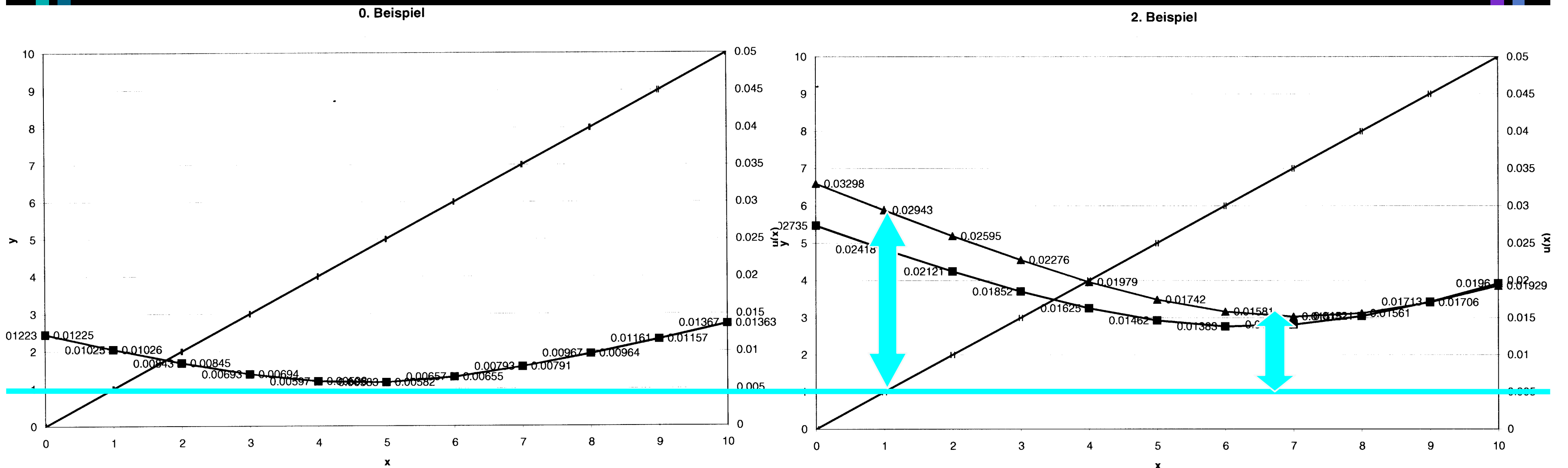
- large uncertainty on reference contributes <u>a lot</u> to uncertainty
- poor control to this reference produces a <u>large</u> deviation

Uncertainty of an amount of substance reference/standard:

- Identity
- Purity
- Preparation

Influence of uncertainty of standards in calibration

- NO uncertainty from standard
- With uncertainty from standard and dilution



M. Rösslein, EMPA 2001

Key Comparison CCQM-K2

MEASURAND : amount content of Pb in natural water

NOMINAL VALUE : 63 nmol/kg

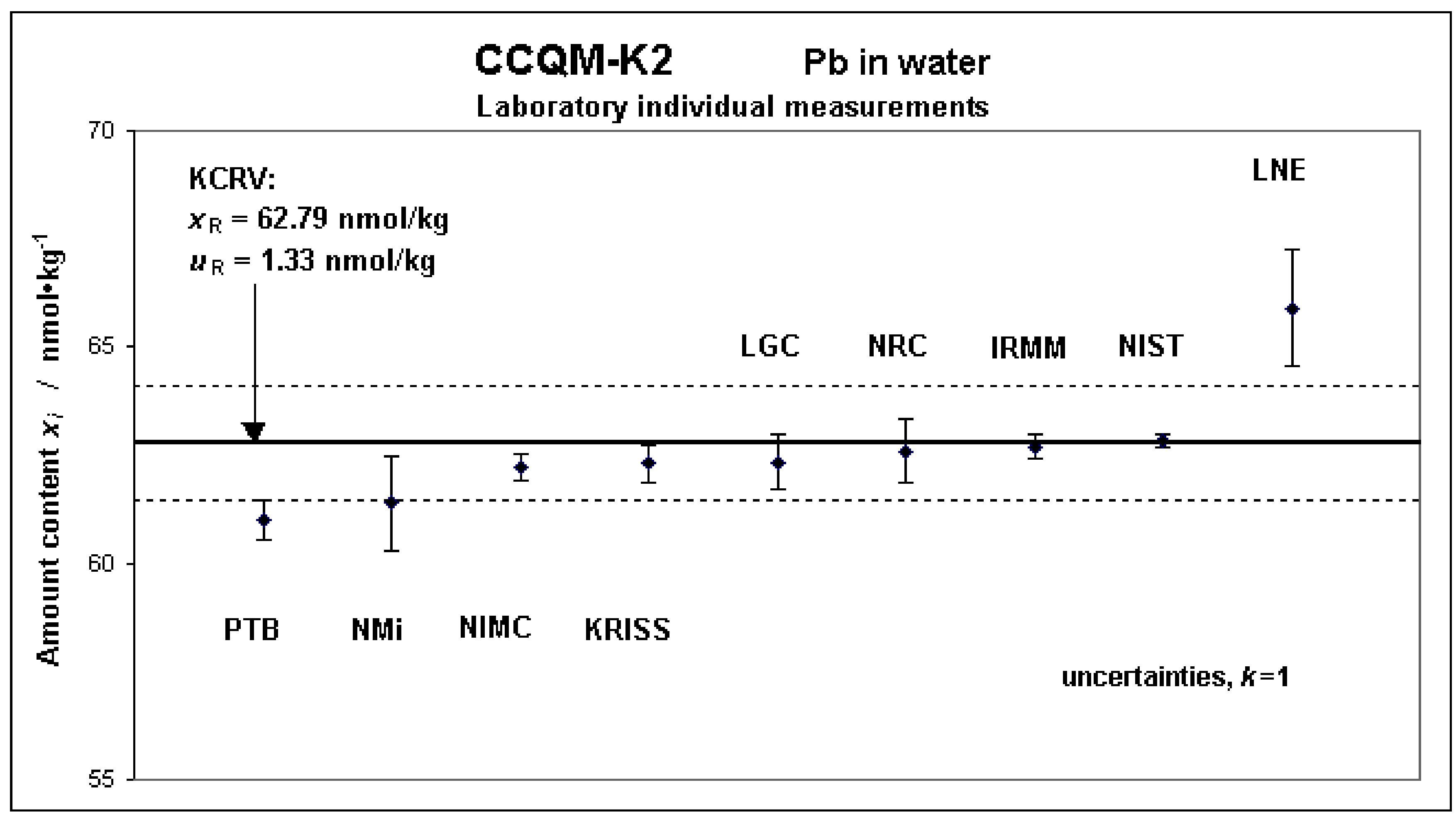
x_i : result of measurement carried out by laboratory *i*

u_i : standard combined uncertainty (k=1) of x_i

Lab *i*	x_i nmol/kg	u_i nmol/kg	Date of measurement
IRMM	62.70	0.26	98-08
KRISS	62.30	0.45	98-08
LGC	62.34	0.62	98-09
LNE	65.90	1.35	98-09
NIMC	62.21	0.30	98-09
NIST	62.84	0.15	98-12
NMi	61.40	1.10	98-08
NRC	62.60	0.75	98-09
PTB	61.00	0.45	98-09

www.bipm.fr

Graph of results:



Source: www.bipm.fr

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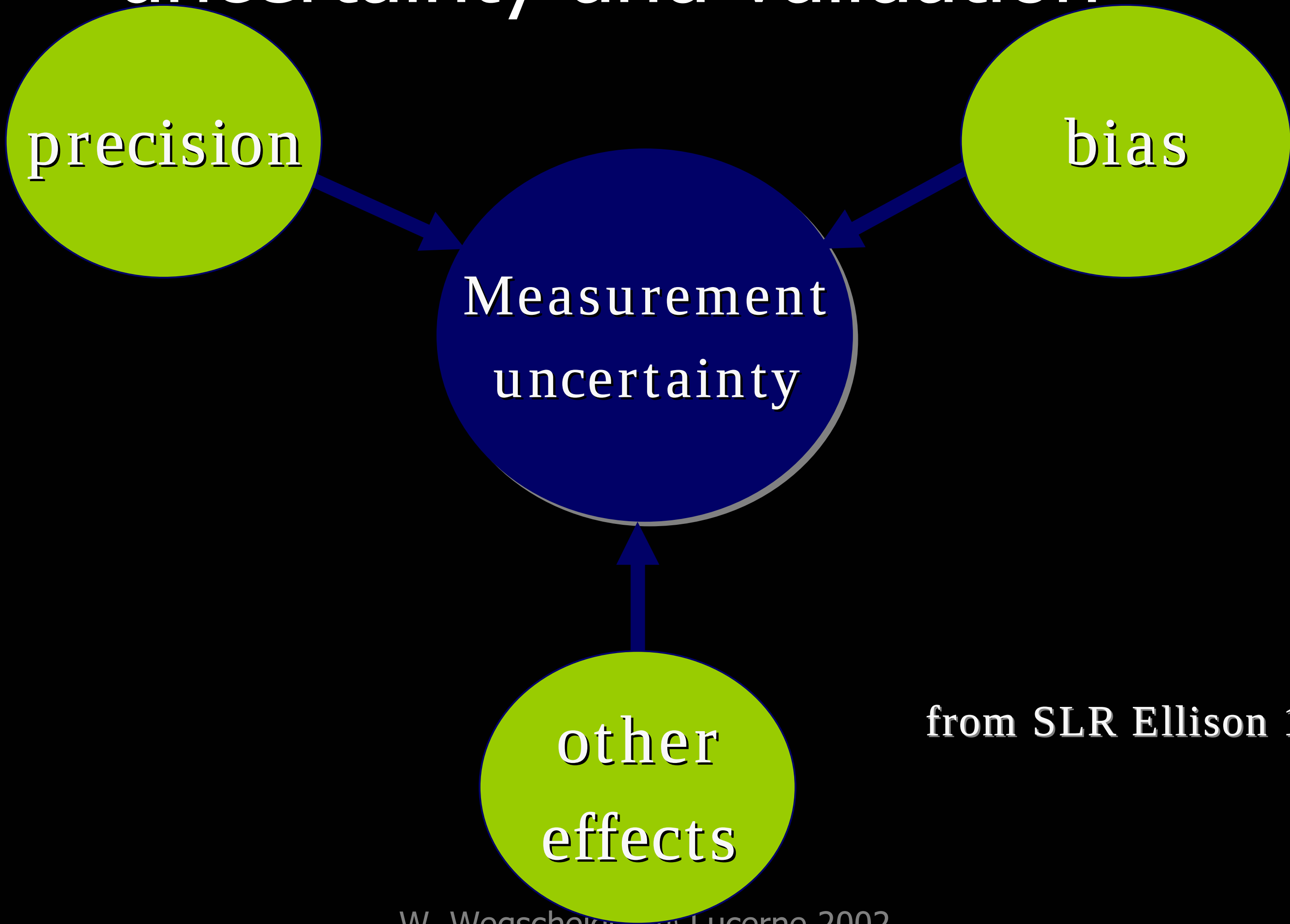
Standard view of the relation between uncertainty and validation



from SLR Ellison 1999

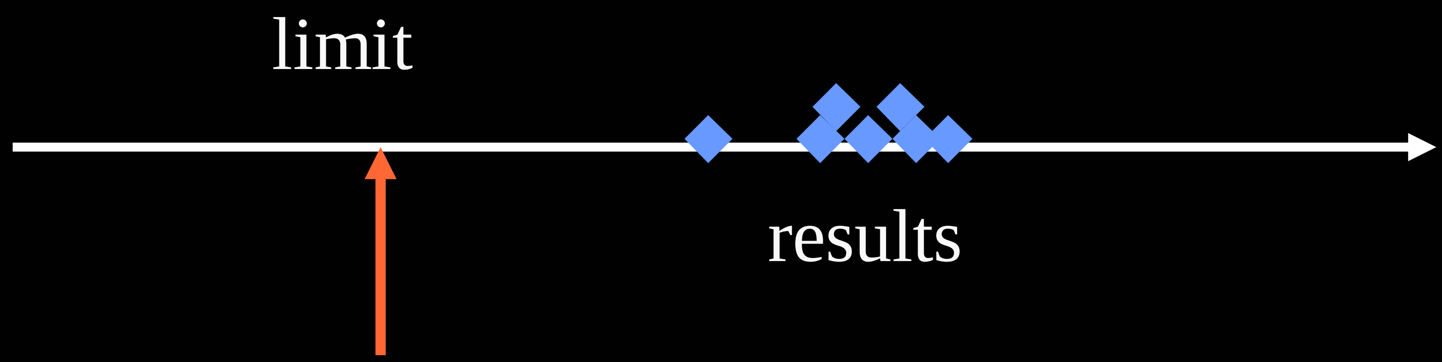
Traditional roles of method validation

- Establish performance characteristics
  - Linearity
  - Limits of detection/determination
  - Precision: repeatability, intermediate reproducibility
  - Effect of concomitants
- Present data for approval of method
- Produce control limits for everyday operation

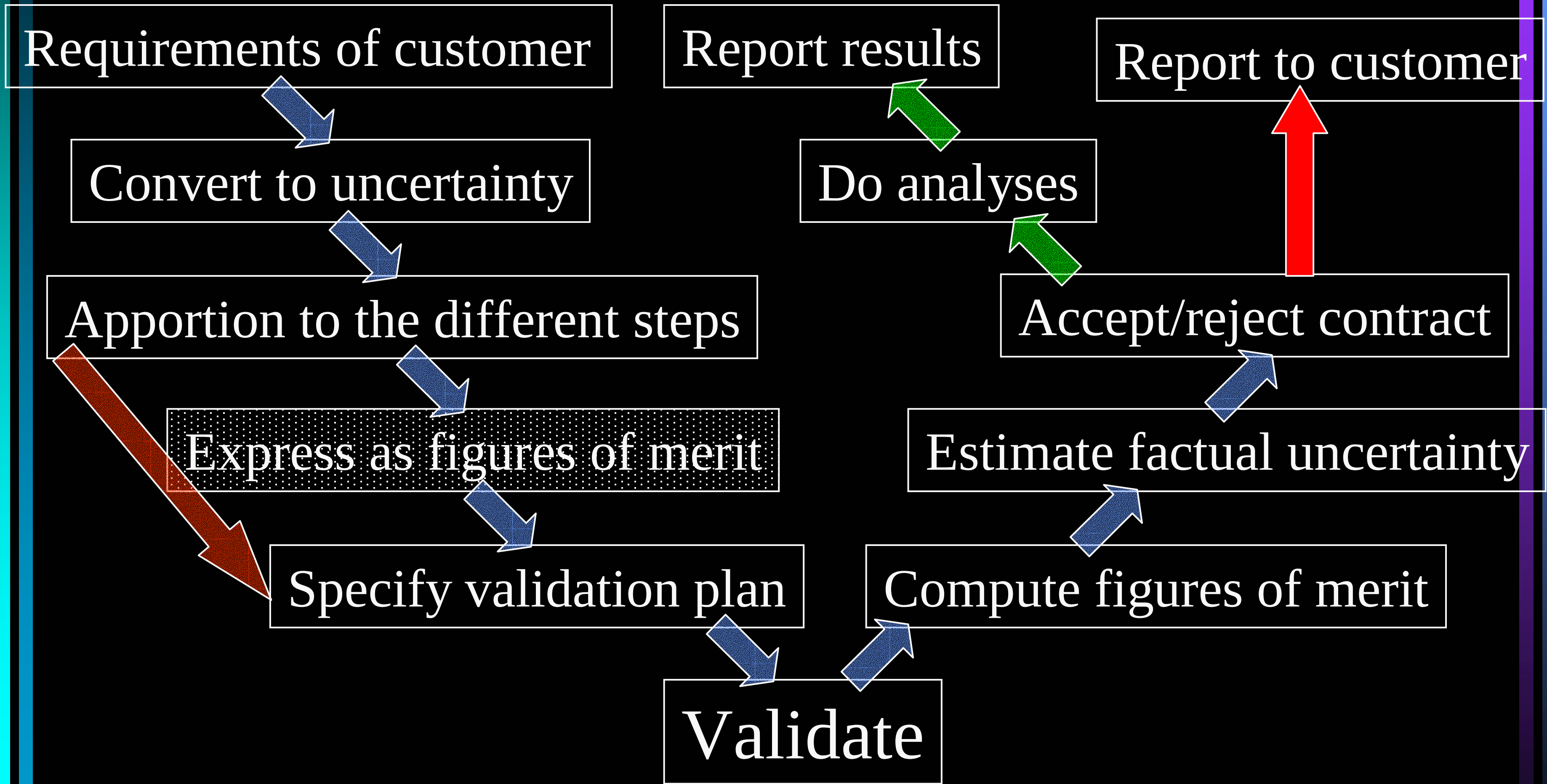
What should be the role of validation ?

As analytical chemistry is about making decisions

- validation should support the decision making process



Validation starts out from the customer´s needs

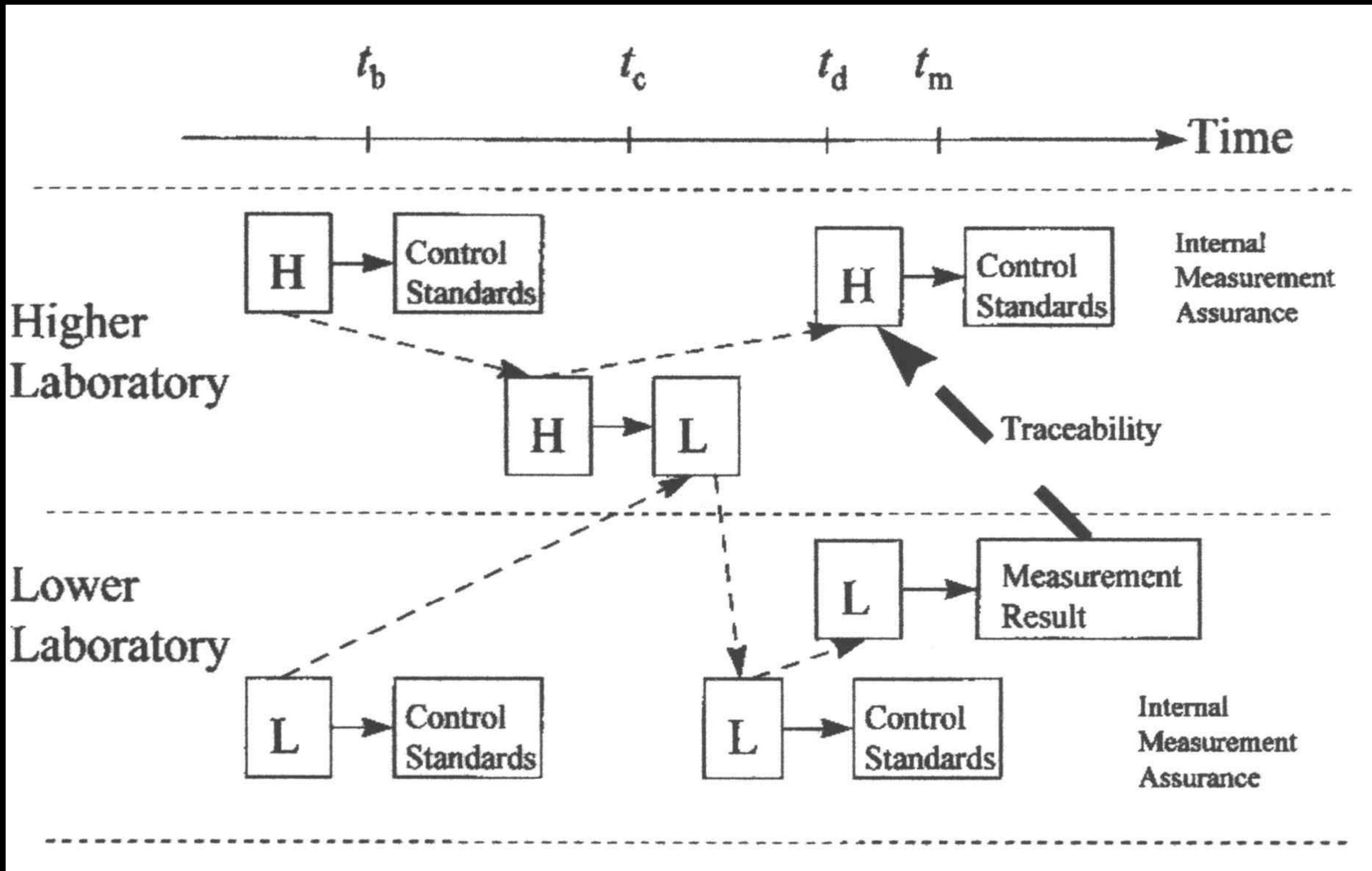


How to achieve stability of references in space and time ?

- Supply standards of high quality to the wider community
- Improve production and measuring skills
- Proliferate preparation and measuring skills
- Be alert to needs for better characterization and production of standards

Metrological Timeline

Ehrlich and Rasberry, 1998



Role of traceability:

- Provide a firm and identical base of units worldwide
- Supply this base in a manner stable in time
- Underpin the hierarchy of measurements/procedures/laboratories
- .....

CITAC

Co-Operation on International Traceability in Analytical Chemistry

- Traceability of results and reference values is a central issue in modern laboratory operation. It is not an end in itself, but serves the purpose of achieving a reliable result.
- Traceability of results can only be claimed if results are accompanied by an uncertainty statement based on traceability of all references, chemical and physical, as well as on procedural contributions to uncertainty.
- A result must be "fit for purpose", thus estimation of measurement uncertainty from uncertainties of references and procedures is added value for laboratories and simple when guidelines are followed.

www.citac.ws