united nations
educational, scientific
and cultural
organization

international atomic
energy agency

the
abdus salam
international centre for theoretical physics

H4.SMR/1503 - 10

WORKSHOP ON NUCLEAR DATA FOR SCIENCE AND TECHNOLOGY: MATERIALS ANALYSIS

(19 - 30 May 2003)

Uncertainty of measurement results in analytical chemistry

Dr. Piotr Robouch
Institute for Reference Materials and
Measurements
European Commission - Joint Research Centre
Geel
BELGIUM

TrainMiC
Training in Metrology in Chemistry

Uncertainty of Measurement Results in Analytical Chemistry

TraInMiC
Training in Metrology in Chemistry

Overview

- **Definitions**
- **Uncertainty - what for?**
- **Limitation of measurements**
- **GUM procedure for uncertainty evaluation**
- **Examples**

TraInMiC
Training in Metrology in Chemistry

When should you evaluate uncertainties of measurement results ?

- When a procedure is introduced inside your laboratory
- When a critical factor changes in the procedure (instrument, operator, …)
- During / together with method validation

➔ An individual evaluation process is NOT needed for every individual result produced !

TraInMiC
Training in Metrology in Chemistry

ISO Definition of Uncertainty

'a parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the *measurand* '

Result = Value ± uncertainty

(22.7 ± 4.8) mg/kg

The value is between 17.9 and 27.5 mg/kg
(cf. *range, interval*)

TraInMiC
Training in Metrology in Chemistry

Why do we need uncertainty?

- It is required by ISO 17025 - Accreditation
- The uncertainty of the result demonstrates the QUALITY of the measurements *(not measuring with the smallest achievable uncertainty)*
- In laboratory → document in transparent way the measurement procedure
- For end-user → give the result with proper confidence
- It improves the knowledge about the measurement procedure
- To allow comparison of results

TraInMiC
Training in Metrology in Chemistry

Why do we need uncertainty ? (2)

- A well documented uncertainty statement underpins your results and provides transparency!
- Your best defence in discussions!
- Repeating the measurement 2, 10 or 100 times does not give you all information to have reliable results!
- Identify major uncertainty contributors -
  find out ways to improve the procedure

TraInMiC
Training in Metrology in Chemistry

True Value or best estimate of True Value

- We can approach to measure the true value by measuring the "the best estimate"

  ➔ aiming to know true value

  - *i.e.* alcohol content of blood
  - *i.e.* nitrate content of drinking water
  - *i.e.* acrylamide content of crisp bread
  - *i.e.* lead content of wine

TraInMiC
Training in Metrology in Chemistry

Are results different?

No results without uncertainty !

R1 = 10.6 mg/kg
R2 = 11.6 mg/kg

- Traditional approach: precision

R1 = (10.6 ± 0.2) mg/kg
R2 = (11.6 ± 0.3) mg/kg

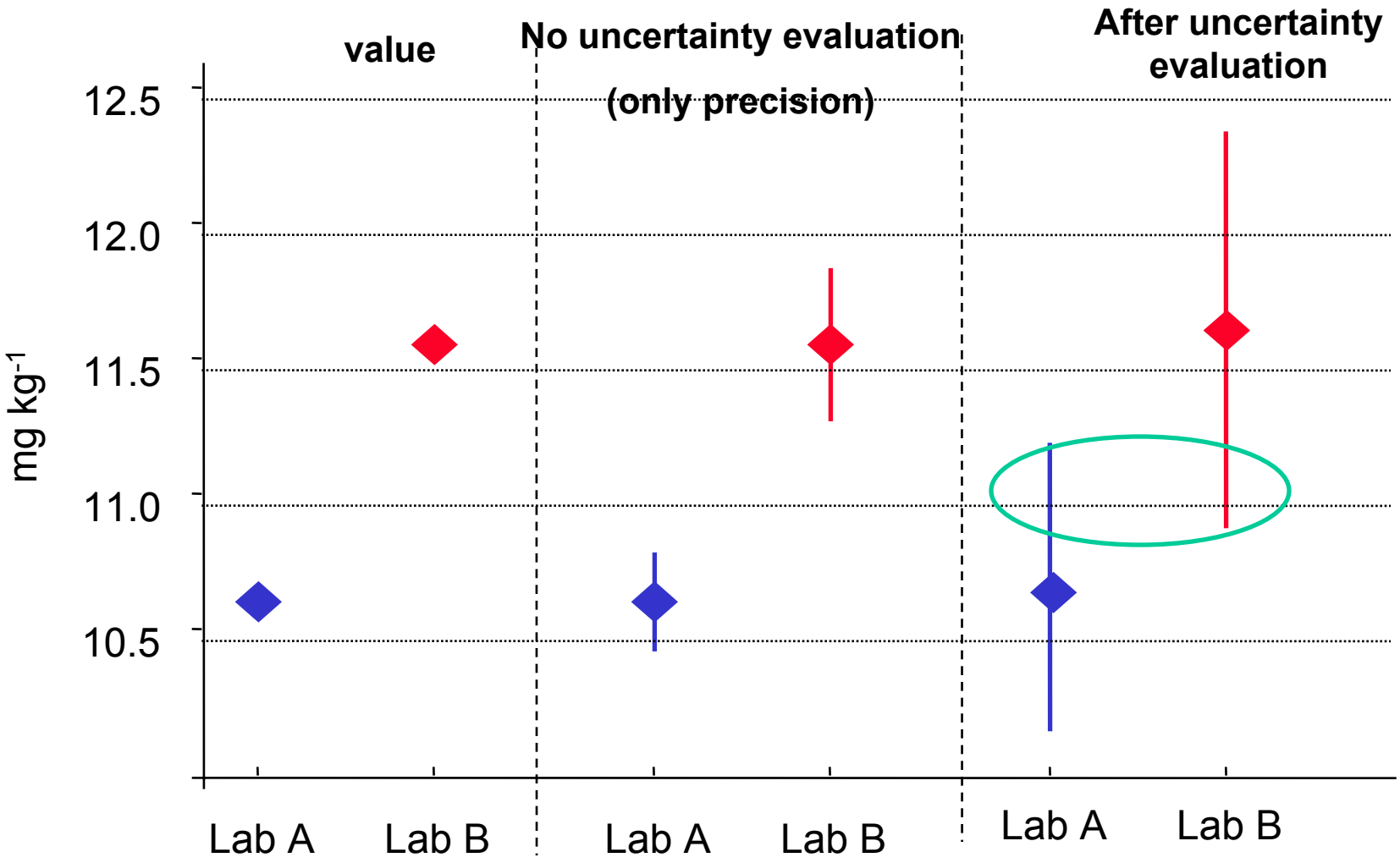
- GUM approach: uncertainty propagation (combined unc.)

to take into account the contribution of all components

R1 = (10.6 **± 0.7**) mg/kg
R2 = (11.6 **± 0.7**) mg/kg

No statistical tests required by GUM *(almost)* …/…
cf. Visual comparison ➔ overlapping ranges Y/N ?

Are these results different?



GUM does not require
statistical tests
unless you need it …

"If it is deemed useful for the intended users of the measurement result, ……, one may indicate - the estimated effective degree of freedom…" – *[GUM 7.2.1]*

- ☑ when comparing results
- ☑ for legal requirements
- ☑ requested by customer

repeatability < reproducibility < combined uncertainty

Don’t forget

What is new in GUM ?

- GUM is guide for a transparent, simple and standardised documentation of the measurement procedure
- Using uncertainty evaluations, such as
  type A (measured in the lab) and *type B (other)*

  Do NOT use random & systematic errors !
- Combined/expanded Uncertainty

TraInMiC
Training in Metrology in Chemistry

Uncertainty "Type"

Type A evaluation of uncertainty:

statistical analysis of series of observations.

Type A standard uncertainty is measured from repeatability experiments and is quantified in terms of *the standard deviation* of the measured values

Type B evaluation of uncertainty:

by *other means* than statistical analysis

(previous experiments, literature data, manufacturer's information)

[GUM, 1993]

TraInMiC
Training in Metrology in Chemistry

Understanding the measurement !

"…The evaluation of uncertainty is neither a routine task nor a purely mathematical one; it depends on detailed knowledge of the nature of the measurand and of measurement…"

[GUM § 3.4.8]

TraInMiC
Training in Metrology in Chemistry

How to apply GUM uncertainty ?

Document the data you used as input for measurement!!

"…The pool of information may include:

- ✓ previous measurement data;
- ✓ validation data
- ✓ experience with or general knowledge of the behaviour and properties of relevant materials and instruments;
- ✓ manufacturer's specifications
- ✓ data provided in calibration and other certificates;
- ✓ uncertainty assigned to reference data taken from handbooks"

[GUM § 4.3.1]

TraInMiC
Training in Metrology in Chemistry

What do you need to know ?

some basic statistics

- average of the set of data;
- standard deviation;
- law of propagation;
- distribution (normal, rectangular, triangular…)

(cf. statistics module)

TraInMiC
Training in Metrology in Chemistry

The 10-steps GUM Sequence

1 - Define the Measurand

2 - Describe the Model Equation *(for the measurement procedure)*

3 - Identify (all possible) sources of uncertainty

4 - Evaluate all input quantities

5 - Evaluate the standard uncertainty (1s) of each input quantities

The 10-steps GUM Sequence
(continued)

6 - Calculate the value of the measurand (using the equation model)

7 - Calculate the combined standard uncertainty of the result

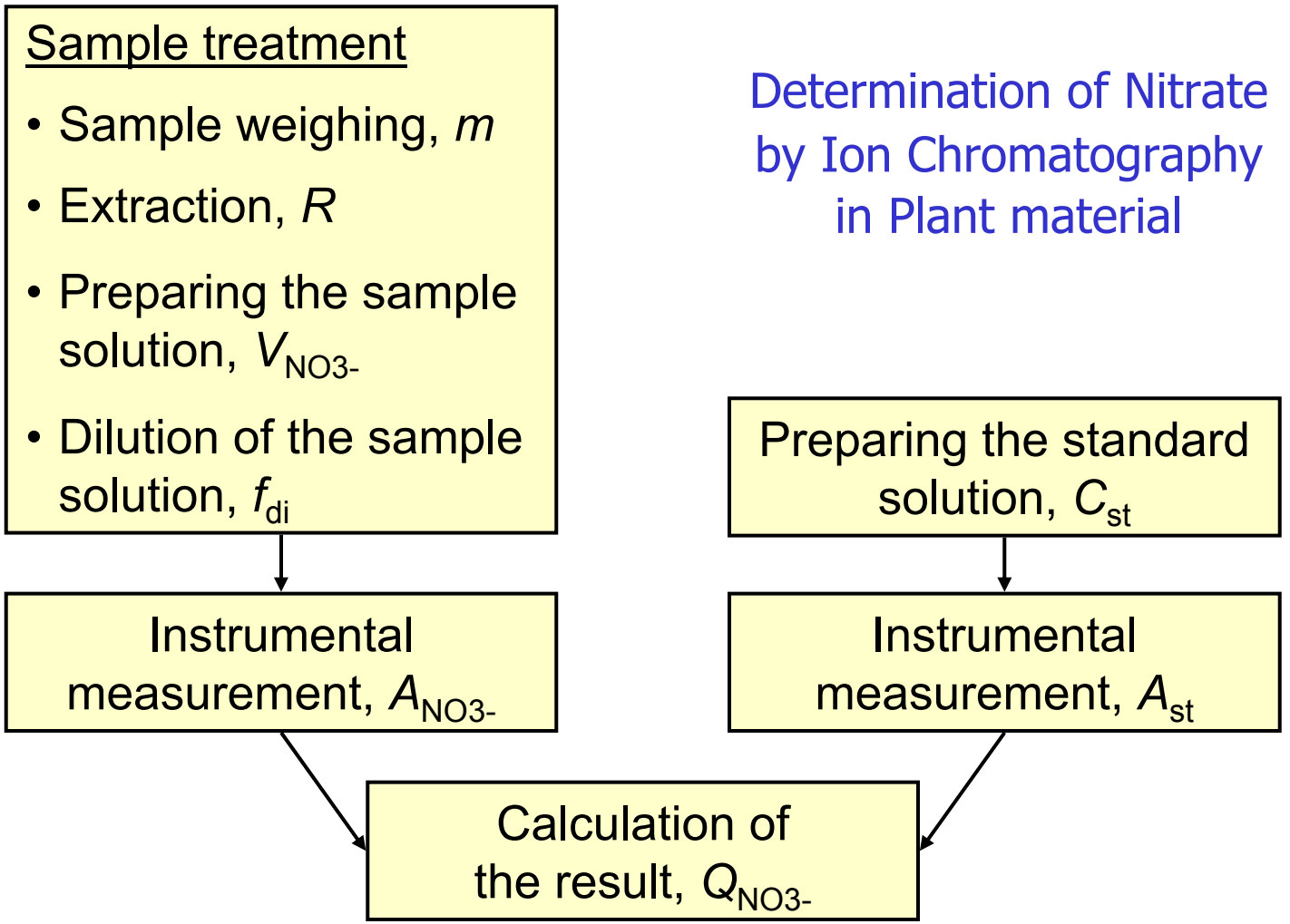
8 - Calculate the expanded uncertainty (with a selected *k*)

9 - Analyse the uncertainty contribution index *(THINK !!)*

10- Document all steps in a Report.

Experimental Protocol

Determination of Nitrate by Ion Chromatography in Plant material



TraInMiC
Training in Metrology in Chemistry

Step 1 - Definition of "Measurand"

Measurand = particular quantity subject to measurement

[VIM 2.6 / GUM B.2.9]

Example: content of NO_3^- in (mg/g)

TraInMiC
Training in Metrology in Chemistry

Step 2 - Model Equation

The model of the measurement procedure is a functional relation between input quantities and output quantity (result)

$$Y = f(X_1, X_2, ..., X_n)$$

Measurement MODEL is the equation you use for the calculation of your result !

You have it already

TraInMiC
Training in Metrology in Chemistry

What are input quantities?

The output quantity Y depends on input quantities $X_1, X_2, ..., X_n$:

$$Y = f(X_1, X_2, ..., X_n) \quad [GUM\ 4.1.2]$$

Input quantities (X_i) may be quantities whose value and uncertainty are directly determined in the current measurement (Type A, *statistical analysis of series of observation*) or brought into the measurement from external sources (Type B, *previous experiments, literature data, information from manufacturer*)

Model Equation

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

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

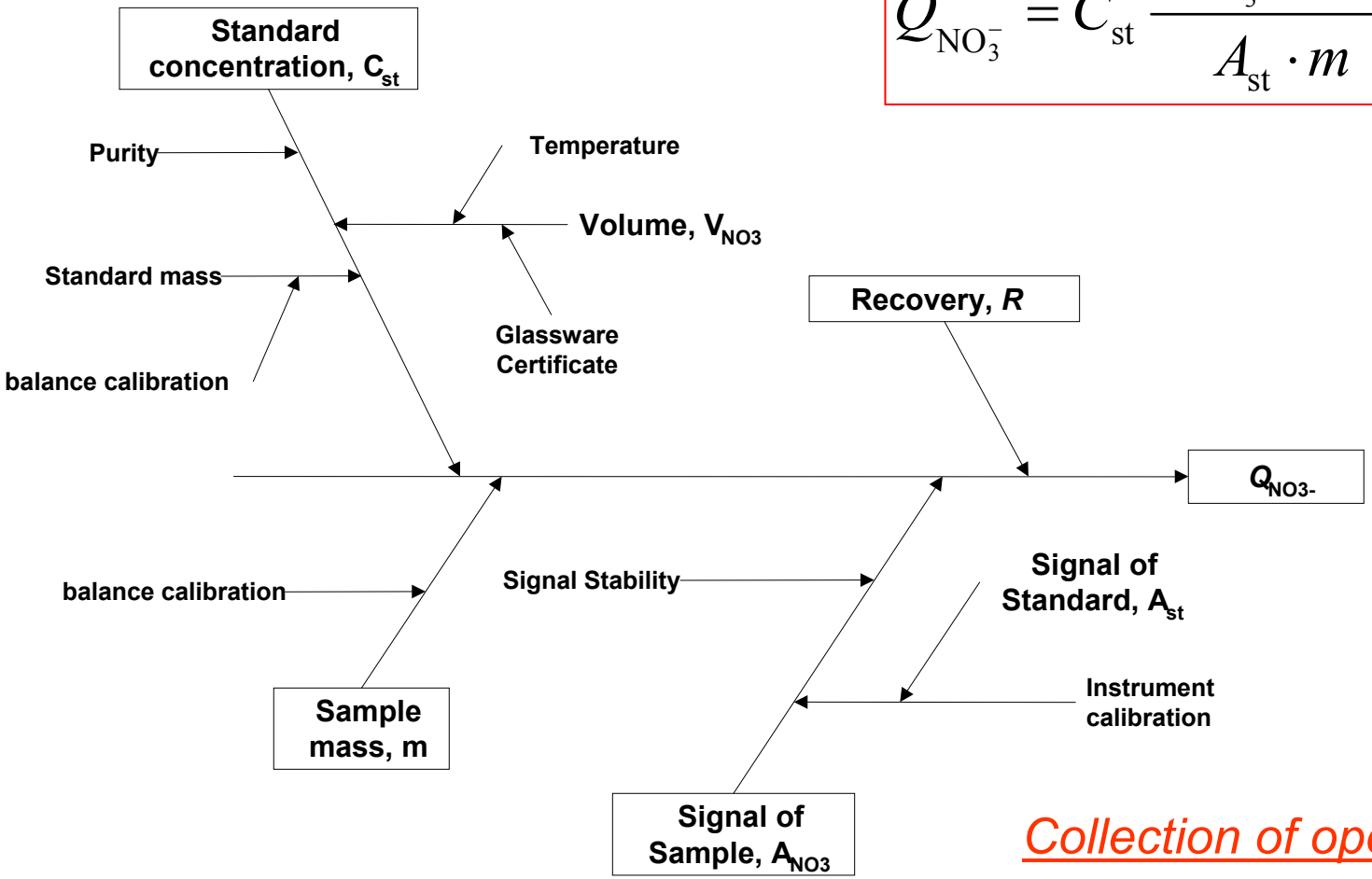
TraInMiC
Training in Metrology in Chemistry

Step 3 - Possible Sources of Uncertainty

- ☑ recovery of analyte from a complex matrix
- ☑ storage conditions
- ☑ reagent purity
- ☑ assumed stoichiometry
- ☑ sampling
- ☑ measurement conditions
- ☑ instrument response
- ☑ bias of instrument
- ☑ instrument resolution
- ☑ uncertainty of standards and CRM's
- ☑ variations in repeated observations

Step 3 - Possible Sources of Uncertainty

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



Collection of operations

TraInMiC
Training in Metrology in Chemistry

Step 4 - Input Quantities Uncertainty (type A & B)

- repeated observation (A)
- validation experiments (A and/or B)
- manufacturers' specifications (B)
- calibration certificates (B)
- results of interlaboratory method validations (B)
- from experience and/or literature (B)

Step 5 - Convert to Standard Uncertainties

Before combining, all uncertainty contributions must be expressed/converted as "estimated" standard uncertainty

when available as:

- standard deviation: use as is
- confidence intervals: convert
- stated range: convert
- expanded uncertainties: convert

See Module "Statistics"

Step 6 - Calculate Value of Measurand

Use model equation to calculate the value of output quantity Y (c_{NO3-})

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

Example

$$Q_{NO_3^-} = 0.801 \times \frac{0.0131 \times 0.1000}{0.0232 \times 1.142} \times 10 \times \frac{1}{0.78}$$

$$\boxed{Q_{NO_3^-} = 0.508 \quad mg / g}$$

Step 7 - Combined Standard Uncertainty

When there is no correlation between input quantities the combined standard uncertainty is evaluated as the square root of the combined variance according to:

$$u_c^2(Y) = \sum \left(\frac{\partial f}{\partial X_i} \right)^2 \cdot \left(u(X_i) \right)^2$$

Law of Uncertainty propagation

where

$u_c(Y)$ = combined standard uncertainty

$u(X_i)$ = standard uncertainty of each input quantity

Can be done by spreadsheet or by dedicated software!

See Module "Statistics"

Combined Standard Uncertainty

$$u_{c,r}(Q_{NO_3^-}) = \sqrt{\begin{aligned} &RSu(C_{st})^2 + RSu(A_{NO_3^-})^2 + RSu(A_{st})^2 + \\ &+ RSu(V_{NO_3^-})^2 + RSu(m)^2 + RSu(f_{di})^2 + RSu(R)^2 \end{aligned}}$$

where $RSu(X_i) = u(X_i)/X_i$ *(relative standard uncertainty)*

$$u_{c,r}(Q_{NO_3^-}) = \sqrt{\begin{aligned} &\left(\frac{0.00058}{0.801}\right)^2 + \left(\frac{0.0003}{0.0131}\right)^2 + \left(\frac{0.0006}{0.0232}\right)^2 + \\ &+ \left(\frac{0.0003}{0.1000}\right)^2 + \left(\frac{0.00058}{1.1420}\right)^2 + \left(\frac{0.023}{10.000}\right)^2 + \left(\frac{0.04}{0.78}\right)^2 \end{aligned}}$$

$$u_c(Q_{NO3-}) = u_{c,r}(Q_{NO3-}) \times Q_{NO3-} = 0.032 \text{ mg/g}$$

TraInMiC
Training in Metrology in Chemistry

Step 8 - Expanded Uncertainty

The expanded uncertainty, U, is obtained by multiplying the combined standard uncertainty $u_c(y)$ by a coverage factor k:

$$U = k * u_c$$

The result is then expressed as: $\boxed{\text{Result} = y \pm U \ (k = ??)}$

For the example: $Q_{NO3-} = (0.51 \pm 0.06)$ mg/g , $k = 2$

- the best estimate of the value attributed to the measurand is "y",
- the interval $[y - U\,,\, y + U]$ is the range that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand.

TraInMiC
Training in Metrology in Chemistry

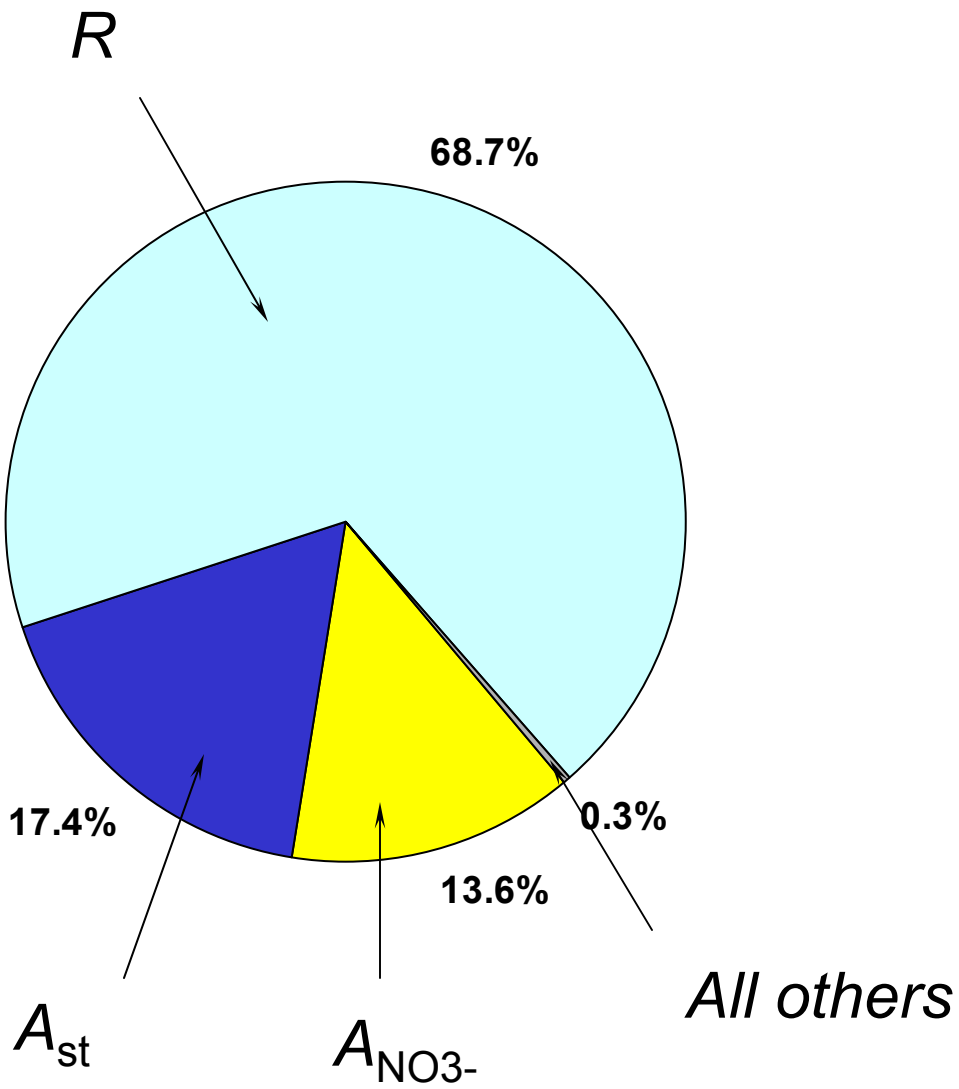
Step 8 - Expanded Uncertainty (2)

- Expanded uncertainty gives a more realistic range of possible values.
- The coverage factor usually used is $k = 2$, representing a coverage of about 95%, if the distribution is normal

Standard uncertainty should be used inside the laboratory
(to apply uncertainty propagation)

Expanded uncertainty is more realistic range
given for the end-users of the results

Step 9 - Uncertainty Contributions



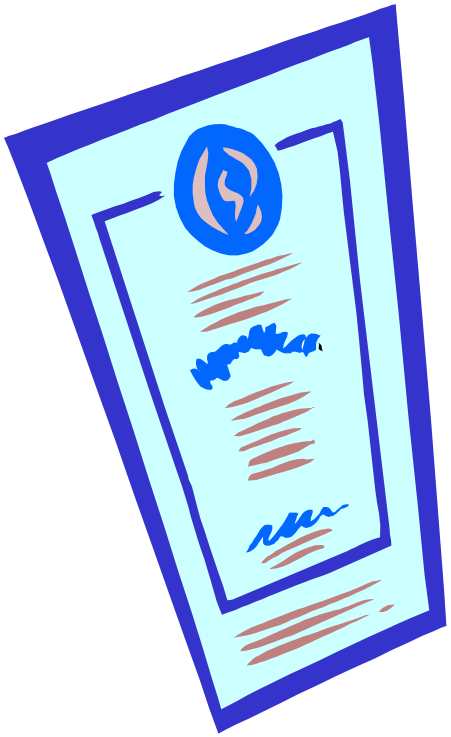
Major Contributor :

- Type B? ☹
- Type A? ☺
- Replicates?
- Much work?
- Control Charts?

Think!

See Module "Statistics"

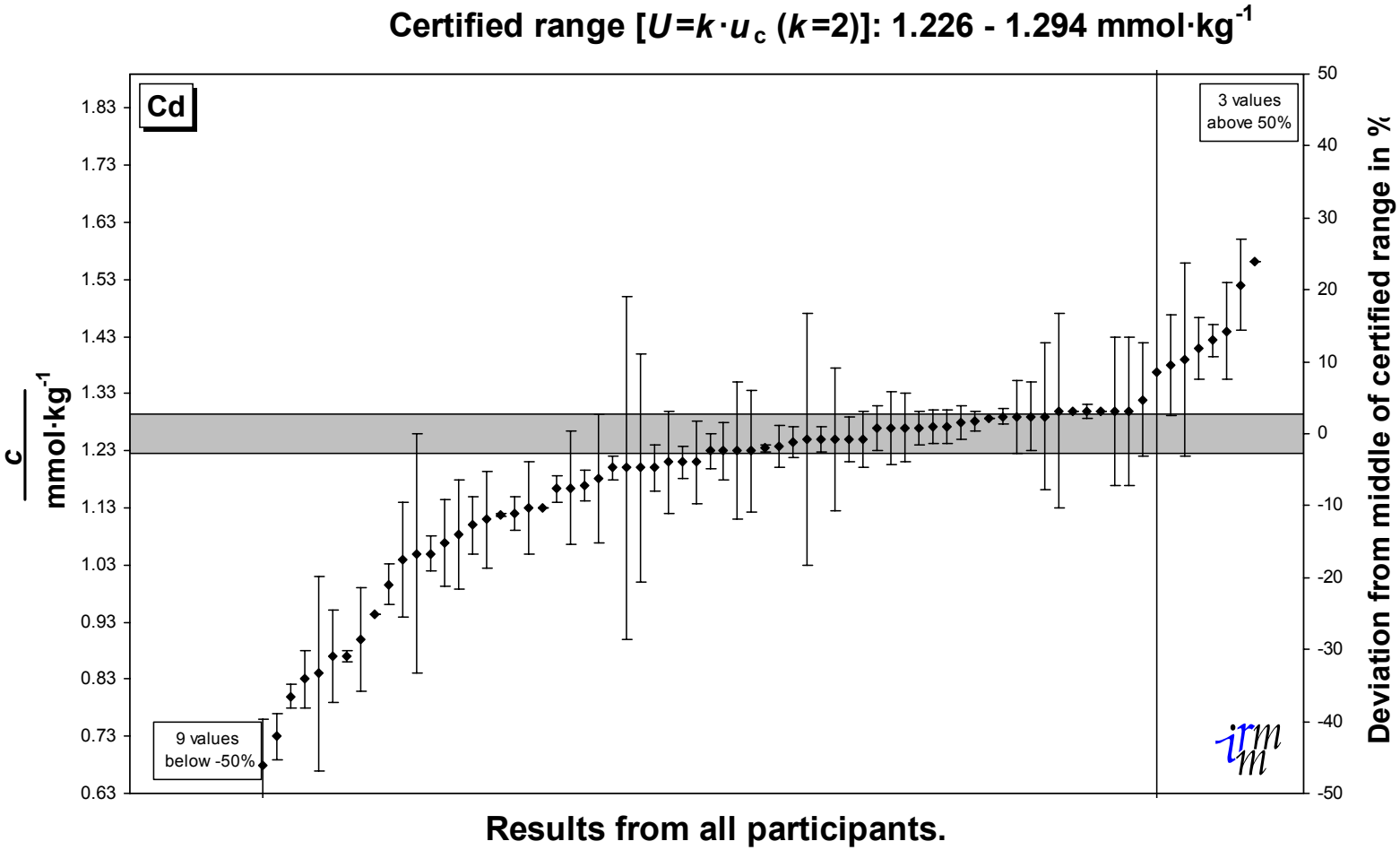
Step 10 - Reporting Results



$$Q_{NO3-} = (0.51 \pm 0.06)\ \text{mg/g}\ (*)$$

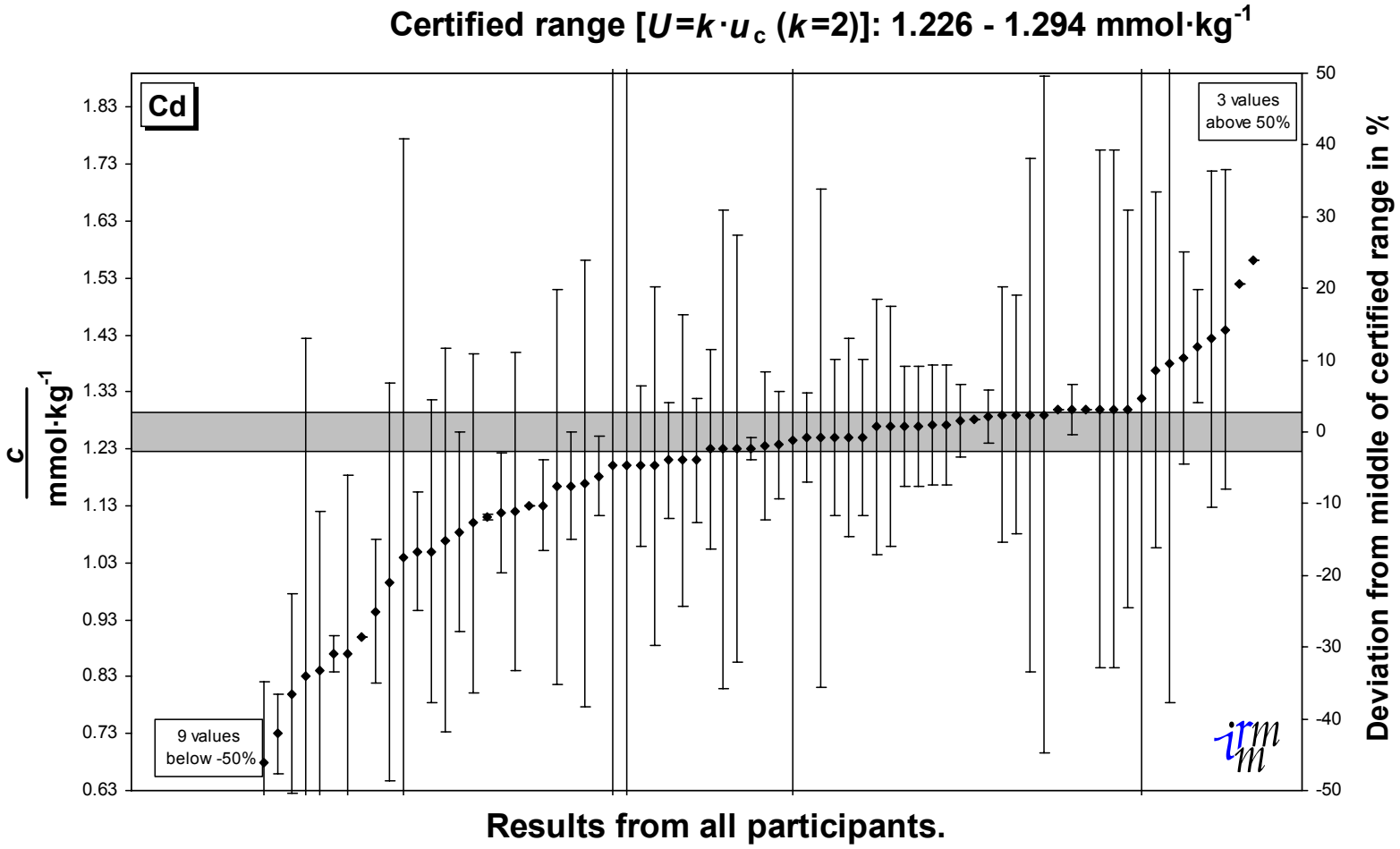
(*)

the reported uncertainty is an expanded uncertainty calculated using a coverage factor of $k = 2$*, which gives a level of confidence of approximately 95%*



Metrologists obsessed by small uncertainties ?

Tra in MiC
Training in Metrology in Chemistry



Learning how to apply GUM:
Better sell your results with
reliable uncertainty statement !

TraInMiC
Training in Metrology in Chemistry

Summary: about uncertainty

- Uncertainty of measurement results evaluation according to the GUM is a useful and accepted concept to evaluate results of a measurement;
- It allows others (e.g. assessors) to understand what & how things were done
- It allows the analyst to combine prior knowledge and observations in a consistent and well defined way;
- It doesn't requires to measure with smallest achievable uncertainty

TraInMiC
Training in Metrology in Chemistry

Uncertainty adopted and accepted by ...

- This concept is adopted and accepted by international institutions, such as NMIs and BIPM
- Is required under ISO 17025 for accreditation
- IUPAC, OIML and accreditation community such as EA and ILAC have accepted this concept
- CEN is working on incorporating typical uncertainties for each procedure