

# DIFFERENT APPROACHES TO ESTIMATION OF MEASUREMENT UNCERTAINTY IN ANALYTICAL CHEMISTRY

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30.09.2010

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## The main question of uncertainty evaluation in an analytical lab:

The uncertainty sources are more or less known

There are different data available (control charts, PT results, parallel measurements ...)

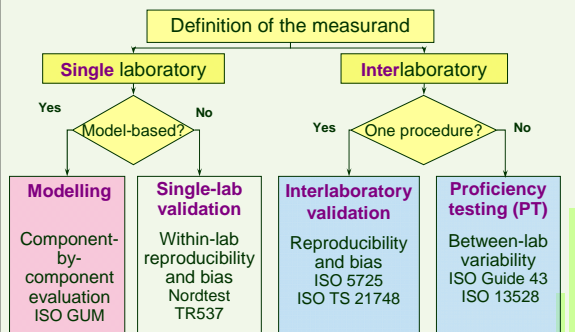
How to use these data to take these uncertainty sources into account?

Different approaches offer different solutions to this question

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## Uncertainty approaches



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## Uncertainty by different approaches

- Modelling (classical ISO GUM)
  - Uncertainty of an **individual result** of a measurement can be obtained
- Single-lab validation
  - Typical uncertainty of results obtained using a **procedure in the laboratory**
- Interlaboratory validation
  - Uncertainty of results obtained using the same **procedure in different laboratories**

These uncertainties refer to different situations

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## Approach based on Modelling

aka "the classical ISO GUM approach"

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## Essence

- Based on measurement model, identification and quantification of all important uncertainty components
- Has been applied in chemistry, but often with problems

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## Challenges with Chemical Measurements

- Often not readily modeled
- Uncertainty contributions not readily quantified
  - Analyte losses during sample preparation
  - Interferences from other components of the sample
  - Sample inhomogeneity
  - Often insufficient information available

**Danger to underestimate uncertainty!**

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## Weighing ...

- “Normal” uncertainty of weighing with a 0.0001g balance is 0.0003 .. 0.0005 g ( $k = 2$ )
- This holds only for “well-behaving” objects!
- **Does not** hold, if:
  - The object is hygroscopic
  - If there is electrostatic charge
  - If the object is volatile
  - Some other cause for unstable reading

**In such cases the uncertainty can well be 10 times higher!**

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## Example: Moisture Content

- The model:

$$Q_{\text{moisture}} = \frac{m_{\text{sample}} - m_{\text{sample\_after\_heating}}}{m_{\text{sample}}} \times 100\%$$

- Substituting typical balance data yields:
- $Q_{\text{moisture}} = (12.500 \pm 0.013) \% (k = 2)$

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## Example: Moisture Content

- If in addition to the balance we try to take into account:
  - Sample inhomogeneity
  - Possibly incomplete drying
- Then, substituting more realistic data, we get:
- $Q_{\text{moisture}} = (12.50 \pm 0.88) \% (k = 2)$

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## Example: Moisture Content

**The difference between 0.013% and 0.88% is almost 70 times !**

**The intrinsic balance uncertainty sources are almost insignificant in this case!**

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**Underestimation of uncertainty is not an “intrinsic property” of the traditional ISO GUM Method**

**It all depends on the implementation**

**But can be very work-intensive**

**Thus, alternative approaches have been developed**

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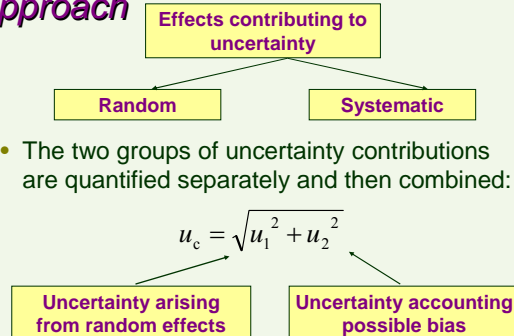
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## Approach based on validation and Quality Control Data

aka "the Nordtest approach"

Nordtest Technical Report 537 (2003)  
<http://www.nordicinnovation.net/nordtestfiler/tec537.pdf>

## Single-laboratory validation approach



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## Single-laboratory validation approach

- In this approach the most important issues are:

**(1) To cover the whole range of effects** arriving with typical use of the measurement procedure, range of expected values and sample types within the scope of the method.

From quality control we obtain **within-lab reproducibility,  $s_{RW}$**

Can be conveniently obtained from an X Control Chart

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## Single-laboratory validation approach

- In this approach the most important issues are:

**(2) To evaluate the bias (estimate of trueness)**  
 the use of certified reference materials (CRMs), comparison with reference methods can be used to evaluate the component of uncertainty related to the **trueness i.e.  $u(\text{bias})$**

If no CRM or reference methods are available also PT can in some cases be used to estimate bias

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## Single lab validation approach: in practice (1)

- The main equation:

$$u_c = \sqrt{u(R_w)^2 + u(\text{bias})^2}$$

Within-laboratory reproducibility  
 This component accounts for the random effects

Uncertainty of the estimate of the laboratory and the method bias  
 This component accounts for the systematic effects

Nordtest Technical Report 537 (2005)  
<http://www.nordicinnovation.net/nordtestfiler/tec537.pdf>

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## Single lab validation approach: in practice

Steps of the process:

- 1\*. Specify measurand
2. Quantify  $R_w$  component  $u(R_w)$
3. Quantify bias component  $u(\text{bias})$
- 4\*. Convert components to standard uncertainties  $u(x)$
- 5\*. Calculate combined standard uncertainty  $u_c$
- 6\*. Calculate expanded uncertainty  $U$

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\* Note – general step – the same for modeling

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**$u(R_w)$**

- $u(R_w)$  is the uncertainty component that takes into account long-term variation of results within lab reproducibility ( $s_{RW}$ )
- Ideally:
  - The same lab
  - The same procedure
  - Different days (preferably over 1 year)
  - Different persons
  - Different reagent batches
  - Sample similar to test samples – matrix, concentration, homogeneity
  - ...

Repeatability < Within-lab reproducibility < Combined uncertainty

$S_r < S_{RW} < U_c$

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**$u(R_w)$**

from:  $u(R_w) = s_{RW}$  is usually found

- the warning limits of X chart
  - using a stable control sample
- long term pooled standard deviation

Ideally: separately for different matrices and different concentration levels!

The control sample analysis has to cover the whole analytical process

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**$u(bias)$**

- The **bias** of lab's results from the best estimate of true value is taken into account
- $u(bias)$  can be found:
  - From analysis of the same samples with a reference procedure
  - From analysis of certified reference materials (CRMs)
  - From interlaboratory comparison measurements
  - From spiking experiments

Ideally: several reference materials, several PTs because the bias will in most cases vary with matrix and concentration range

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**$u(bias)$**

$$u(bias) = \sqrt{RMS_{bias}^2 + u(C_{ref})^2}$$

This component accounts for the average bias of the laboratory results from the  $C_{ref}$

This component accounts for the average uncertainty of the reference values  $C_{ref}$

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**$u(bias)$**

- The averaging is done using the **root mean square**:

$$RMS_{bias} = \sqrt{\frac{\sum (bias_i)^2}{n}}$$

$$u(C_{ref}) = \sqrt{\frac{\sum u(C_{ref}_i)^2}{n}}$$

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**Uncertainty due to possible bias**

Evaluation of uncertainty due to bias, ideally:

- Separately for different sample matrices
- Separately for different concentration levels

This approach is rather demanding in terms of availability of sample data

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## Single lab validation approach: Determination of ammonium in water

- According to EN/ISO 11732
- Concentration level 200 mg/L
- From the X chart: warning limits are set to  $\pm 3.34\%$ 
  - Warning limits are set to 2s
  - Thus  $u(R_w) = 3.34\% / 2 = 1.67\%$

Example from: Nordtest Technical Report 537 (2003)  
<http://www.nordicinnovation.net/nordtestfiler/tec537.pdf>

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## Single lab validation approach: Determination of ammonium in water

- From the interlaboratory comparison results bias over 3 years has been: 2.4%, 2.7%, 1.9%, 1.4%, 1.8% and 2.9%.
  - Thus  $RMS_{bias} = 2.25\%$
  - Uncertainty of nominal values is estimated as  $u(Cref) = 1.5\%$
  - Thus  $u(bias) = 2.71\%$
- Standard uncertainty:
 
$$u_{bias} = \sqrt{2.25^2 + 1.5^2} = 2.71\%$$

$$u_c = \sqrt{1.67^2 + 2.71^2} = 3.18\%$$
- Relative expanded uncertainty:  $U = 6.4\%$

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## Interlaboratory Approaches

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## Interlaboratory validation approach (1)

- The main uncertainty sources can be taken into account via the between-lab reproducibility

Main equation:

$$u_c = s_R \quad U = 2 \cdot u_c$$

$s_R$  is between-lab reproducibility

ISO 5725 Accuracy (trueness and precision) of measurement methods

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## Interlaboratory validation approach (2)

- Data from different labs on the analysis of **the same sample** carried out by **the same procedure**
- The  $s_R$  values are often given in standards (e.g. ISO)

### Main limitation:

This approach completely ignores the situation at a specific laboratory

Suitable for very standardized procedures or as a rough estimate

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## Approach based on the results of PT-s

- The standard deviation of the participant results in a PT  $s_{PT}$  can be used as a **very rough initial estimate of  $u_c$**
- Usually different procedures are used by different labs in PT-s

This is not a recommended approach.  
 Usable just for obtaining the preliminary rough guess.

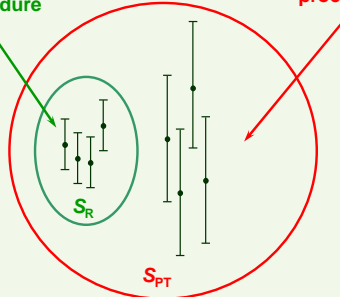
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## Between-lab spread of results

Labs use the same procedure

Labs use different procedures



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## Comparison of the approaches, Additional aspects

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## Comparison of the approaches

### Modelling

- Advanced laboratories
  - Extra work usually required
  - Deep knowledge required
- Danger to underestimate uncertainty
- Promotes **thinking**, high value in **teaching**

### Single-lab validation

- Routine laboratories
  - Lots of data needed
  - Less extra work** required
- Realistic uncertainty estimates
- Teaching value is lower than with modelling

### Interlaboratory validation

- Minimal work or knowledge required
- $S_R$  value has to be known
- Crude uncertainty estimates

### PT approach

- Minimal work or knowledge required
- Very crude uncertainty estimates
- Should be used only as first approximation

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## Comparison of different approaches

Ammonium in fresh water – low levels 0,2 mg/L  
According to ISO 7150-1 or EN-ISO 11732

based on ...

Modelling	Single-laboratory validation	Interlaboratory data	Proficiency testing
≈ 7 % (*)	≈ 7 % (**)	≈ 16 % (**)	18 – 22 % (**)

(\*) Expanded uncertainty with comprehensive analysis of uncertainty sources  
(\*\*) Typical expanded uncertainty values

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## Absolute vs relative uncertainties

- Rules of thumb:
  - At low concentrations (near detection limit, trace level) use absolute uncertainties**
    - Uncertainty is not much dependent on analyte level
  - At higher concentrations use relative uncertainties**
    - Uncertainty is roughly proportional to analyte level

Appendix E.4 from Quantifying Uncertainty in Analytical Measurement, EURACHEM/CITAC Guide, Second Edition (2000)  
Available from : <http://www.eurachem.org/>

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## Choosing the approach

- If you have
  - Competence and time
  - Data on all important influencing quantities
    - Use the Modelling approach
- If you have
  - Quality control data and results of participation in ILC-s
    - Use the Single-lab validation approach
- If you are using a highly standardized procedure within its scope
  - Use the Interlaboratory validation approach

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## Credits

- This presentation has been created in collaboration with **Bertil Magnusson** (SP, Sweden)
- Part of this presentation has been used in the



training materials