THE CHALLENGE OF ESTIMATING UNCERTAINTIES

(to allow proper conclusions to be drawn)

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INTRODUCTION

- About metrology

UNCERTAINTY ESTIMATION PROCESS

- Specification of the measurand
- Identification and quantification of uncertainty sources
- Calculation of the final combined uncertainty

MEANING AND USE OF UNCERTAINTY

- Levels of confidence
- Comparison between different measurement results: discrepancy and agreement

FINAL REMARKS

INTRODUCTION

Viewpoints about measurements

STATISTICAL

it is always possible to find the adequate statistical model to describe the system. The systematic effects are viewed as correlation between measurements results

LEGAL

it is important to have the highest level of confidence in the measurement results

METROLOGICAL

it is necessary to have the maximum knowledge of the measurement system in order to know how to reduce the uncertainty

ENGINEERING

it is important to choose the measurement method and model suitable with the application required

"...when you can measure what you are speaking about, and express it in numbers, you know something about it; but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meager and unsatisfactory kind…"

(Lord Kelvin)

The **true value** of a quantity is unreachable, because would be obtained by a **perfect** measurement.

Measurements are inherently **variable**

The result of a **real** measurement is an **estimate** of the true value

A complete statement of the **measurement result** must include its **uncertainty**

Accuracy: closeness of a measurement result with the true value

Uncertainty: parameter that characterizes the dispersion of the measurement results.

Stability: variability of quantities involved in the measurement

Repeatability: agreement between successive measurement *in the same conditions*

Reproducibility: agreement between measurements *in different conditions*

Sensitivity: minimum detectable quantity

Resolution: distance between two values of the measurand which can be considered *different* (1/2 LSB)

UNCERTAINTY ESTIMATION PROCESS

Specification of the measurand

- What is being measured: a correct definition of the quantity often indicates the needed procedure
  - *range* of values
  - min required *accuracy* and / or max allowed *uncertainty*
  - measurement duration

- ***Influence quantities***: their role is especially important to evaluate systematic effects.

- Method:
  - ***Rational***, when the result doesn't depend on the method
  - ***Empirical***, when the measurand is defined by the measurement method

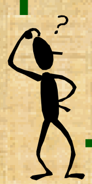
Identifying uncertainty sources
(which are not necessarily independent)

It is important to recognize all the sources of uncertainty in the system and decide which ones are to be taken into account, given the context in which the measurement is required.

Components less than a third of the largest don't (in general) need to be evaluated in detail

Identifying uncertainty sources

- **Sample** → Sampling strategy (random, stratified…); Sample preparation; Storage conditions
- **Calibration** → Uncertainty of the CRM*, Calibration errors (stability between measurements); Instrument accuracy (linearity throughout the scale extension and zero offsets)
- **Measurement process** → Operator effects; Rounding and averaging; Instrument parameters settings
- **Environment** → Temperature, humidity pressure… (stability during measurement time)



*Certified Reference Material

Example: direct density measurement of ethanol (EtOH)

$$d_{EtOH} = \frac{\left(m_{gross} - m_{tare}\right)}{V}$$

Figure D1: Initial list

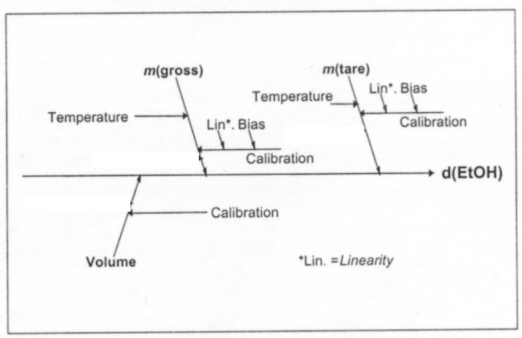


Figure D2: Combination of similar effects

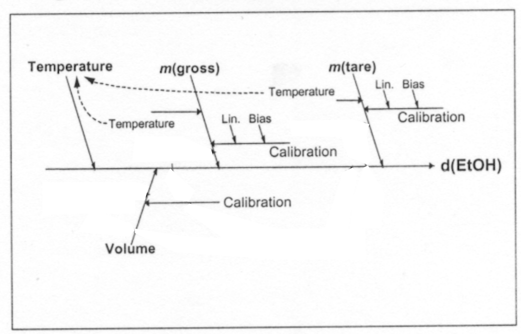
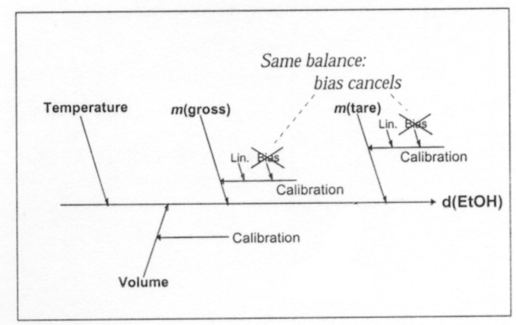


Figure D3: Cancellation



Temperature:

- accuracy of thermometer ΔT_1
- stability and accuracy of temperature controller ΔT_2

Calibration linearity:

- mass
- volume (if the CRM is in other position in the scale)

Calibration bias:

- volume

Quantification of uncertainty

- Combining uncertainties from **each individual source**
- Method performance data or **method validation**
- Uncertainty for **empirical methods**
- Uncertainty at the **detection limit**

Uncertainty

TYPE A
(statistical)

- known statistical properties
- Multiple, independent observations of the measurand
- may be improved increasing the number of observations

TYPE B
(systematic)

- knowledge of the measurement system
- applicable with few observations
- cannot be improved increasing the number of observations

Uncertainty

TYPE **A**

(statistical)

repeatability

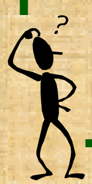
TYPE **B**

(systematic)

bias

Individual sources of uncertainty

- Experimental estimation
  - Type **A**: ***repeatability***
  - Type **B**: systematic variation of parameter(s). Such variation should be sufficient to produce variation of the measurand of the order of 5σ
- Standing data (meas and cal certificates) type B
- Modeling from theoretical principles type B
- Experience judgement



Combined uncertainty from method performance data

Relevance of prior studies ⇨
- Comparable (type **A**)
- Use of bias data are justified (type **B**)

It is general requirement of the ISO guide that corrections should be applied for all recognized and significant systematic effects (type **B** or **bias**).

with respect to the (combined) uncertainty estimated *without* the bias

bias **uncorrected** by convention
⇓
empirical method

- Certified Reference Materials

is a **calibration**
of the whole measurement
against a **traceable reference**.
(**A** and **B**)

- collaborative study

σ_R *reproducibility* standard deviation (**A** and **B**)

Dependence of σ_R on level of response
(linear estimate)

Estimate of bias based on CRM (**B**)
(no additional allowance if not significant)

- in-house study

typical sample over time in different conditions
several samples

level dependent contributions

overall bias
- CRM ⇒ combined u_{CMR} and u_{bias}
- reference method ⇒combined u_{ref} and u_{diff}

Combined uncertainty
from
method performance data

Empirical methods

- the associated **bias** is *defined* as **zero**
- bias evaluations refer only to lab performance
- CRM should be considered only if certified with the same method
- overall bias control is done through method parameters control
- collaborative studies

Detection limit

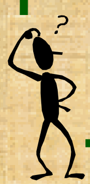
- presence of noise or unstable baseline
- interferences
- losses during preparation may be significant

→ uncertainty increases

→

- laws of propagation of uncertainties may cease to apply

- quantitative (absolute) measurements should not be made
- observations may appear *“unphysical”* (negative concentrations)



Determination of final uncertainty

All uncertainty contributions must be expressed as **standard deviations**

- given a population of ***n*** samples: $\sigma = \sqrt{\sum_{i=1}^{n} \frac{\left(x_i - \overline{x}\right)^2}{n-1}}$

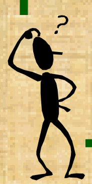
  $\sigma_{mean} = \frac{\sigma}{n}$

  only if Gaussian

- given interval limits $\pm$ ***a***:

  with level of confidence ⇒ normalize with respect to a Gaussian

  without level of confidence ⇒ rectangular / triangular



Determination of final uncertainty

Independent contributions: $\sigma = \sqrt{\Sigma_i (ci\,\sigma_i)^2}$

Not independent contributions: $\sigma = \sqrt{\Sigma_i (c_i\,\sigma_i)^2 + \Sigma_{j,k}(c_i\,c_k\,cov_{ik})}$

$$\sigma^2 = \sigma_A^{\,2} + \sigma_B^{\,2}$$

MEANING AND USE OF UNCERTAINTY

Levels of confidence

Most scientific publication specify uncertainty at the 68% level of confidence.

Nonetheless, a coverage factor ***k*** is considered

•In presence of statistical observation with **few degrees of freedom** (***k***=2)

•When a **higher confidence level** is required by the application (legal metrology with ***k***=2 or 3)

Discrepancy and agreement

$x_{est} \pm u_x$

$y_{est} \pm u_y$

With known level of confidence
Assuming Gaussian population: ⇨ $x_{est} \pm \sigma_x$

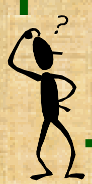
quadrature sum

$\frac{\text{Diff}}{\text{sig}}$

1 ⇒ 32%

2 5%

3 0.3%



Few final remarks

- Knowledge of statistical character of the population

- Stationarity of statistical processes

- Traceability to a known reference

Bibliography

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http://www.bipm.fr/enus/

Publications:

- EURACHEM/CITAC, ***"Quantifying Uncertainty in Analytical Measurement "***, 2000
- ***"Guide to the expression of uncertainty in measurement "***, ISO Geneva, 1993