

# ISO GUM Uncertainty in Chemistry:

## Successes and difficulties

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## Measurement result

- This way of writing:

The benzene content of a fuel is  
 $C_{\text{benzene}} = (32 \pm 6) \text{ mg/kg}, k = 2, \text{ norm.}$

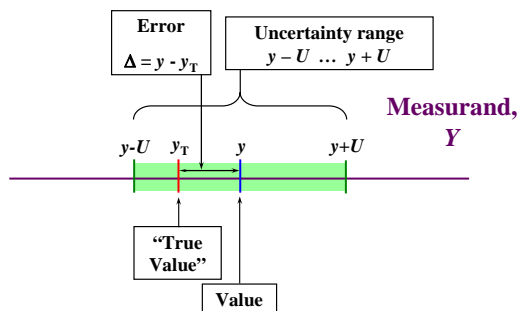
- Is a **measurement result** and means the following:  
The “true” content of benzene in the fuel is in the range of 26 ... 38 mg/kg with probability 95% (in the case of Normal distribution!)

VIM – International Vocabulary of Basic and General Terms in Metrology, ISO, 1993

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## Value, error and uncertainty



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## Measurement uncertainty

- **Measurement uncertainty (or simply uncertainty)** is a parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand

VIM – International Vocabulary of Basic and General Terms in Metrology, ISO, 1993

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## Uncertainty is useful/needed:

- To estimate the reliability of the measurement result
- To be able to compare two measurement results
- To establish traceability
- With uncertainty analysis one has to thoroughly analyze the method
- Information is obtained for improving the method

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## Some basic points:

- **One of the most important things is the common sense!**
- Use all the available information

Very often the uncertainty estimation method is chosen based on the availability of information!

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## Some basic points:

- For some very standardised methods it is prescribed what the uncertainty will be
- but this applies only to **very standardised** methods

**Normally uncertainty cannot be abstracted from the working practices of a particular laboratory!**

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## Uncertainty sources

- When estimating uncertainty all (important) **uncertainty sources** have to be taken into account

*A Very Good Checklist is available in:*

*Quantifying Uncertainty in Analytical Measurement*, 2nd ed.; Ellison, S. L. R.; Röslein, M.; Williams, A., Eds.; EURACHEM/CITAC, 2000.

Available from the web: <http://www.eurachem.ul.pt/>

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## Uncertainty sources

- Uncertainty sources:
  - Sample preparation
    - Sample inhomogeneity
    - Extraction of analyte from the sample is not complete
    - Analyte may partially decompose
    - Analyte may have some volatility and escape from the sample
    - Analyte may adsorb on the walls of the vessels and tubing
    - Sample contamination

**Sample preparation is often one of the most important!**

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## Uncertainty sources

- Calibration of the instrument
  - The standards/etalons have uncertainties
  - The calibration process introduces some uncertainty
- The measurement itself
  - Repeatability of the measurement
  - Drift of the instrument parameters
  - Sample carryover
  - Interference caused by incomplete selectivity
  - Incomplete knowledge of the influence of the environmental conditions

*More:*

*Quantifying Uncertainty in Analytical Measurement*, 2nd ed.; Ellison, S. L. R.; Röslein, M.; Williams, A., Eds.; EURACHEM/CITAC, 2000.

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## Uncertainty sources

- All these sources have to be considered
- Those that have influence have to be **quantified**

**This is often the most difficult thing with chemical analysis!**

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## ISO GUM Method for uncertainty estimation

- The ISO method, published in the

*ISO Guide to Expression of Uncertainty in Measurement - ISO GUM*

- is currently a standard method for uncertainty estimation

*Guide to the Expression of Uncertainty in Measurement*; BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML; ISO: Geneva, 1993.

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## ISO Method with chemical measurements

- Interpretation of the ISO Guide for chemists has been published by Eurachem and CITAC
- The next issue is being worked on
- Currently this is the best material about the ISO method for chemists

*Quantifying Uncertainty in Analytical Measurement*, 2nd ed.; Ellison, S. L. R.; Röslein, M.; Williams, A., Eds.; EURACHEM/CITAC, 2000.

Available from the web: <http://www.eurachem.ul.pt/>

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## The Steps

- The ISO method involves the following steps:
  1. Define the measurand
  2. Build the model equation
  3. Identify the sources of uncertainty
  4. (If necessary) Modify the model
  5. Evaluate of the input quantities and calculate the value of the result
  6. Estimate the standard uncertainty of input quantities
  7. Calculate the combined standard uncertainty of the result
  8. Present the result (as std or expanded uncertainty)
  9. Analyse the uncertainty contributions

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## The ISO Method in Physics

- Well established
- Gives normally good results
  - Physical measurements can usually be well modelled
  - Quantifying the uncertainty sources is generally not very difficult

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## Problems with Chemical Measurements

- Not as readily modelled
- Definition of the measurand can be problematic
- Uncertainty contributions not readily quantified
- It is often difficult to separate the analyte from the matrix
- There are interferences from other components of the sample
- Sample inhomogeneity

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## Does ISO GUM Consistently Underestimate Uncertainty?

- It is sometimes claimed that ISO GUM gives underestimated uncertainties for chemical measurements
- Rob G. Visser (*Accred. Qual. Assur.* **2002**, 7, 124):

“ ... the classic bottom-up approach is not likely to give analytical chemists a helpful tool in the estimation of the uncertainties.”

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## Does ISO GUM Consistently Underestimate Uncertainty?

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

**It all depends on the implementation !**

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## Intrinsic Limitations

- Only Established and validated methods
- It is in principle assumed that all systematic effects are corrected for
- If the method has been validated assuming that there are no interferences, then it should be used under conditions where there are no interferences
- Gross errors are not taken into account

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## Most of the examples that we find are about...

- ... Weighing
- ... Uncertainties of pipette and volumetric flask volumes
- ... Uncertainties of absorbance values

Here the ISO Method is in general doing well!

However ...

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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 is almost 70 times !

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

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## Pipetting ...

- “Ideal” uncertainty of pipetting with a calibrated Mohr pipette is in the order of magnitude 0.1 % ( $k=2$ ) of the volume
- This holds, if:
  - The pipette has been freshly cleaned
  - Pipetting is done carefully
  - The liquid is similar to the one used in calibrating

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## Pipetting ...

- This **does not hold** if:
  - There remain liquid drops on the pipette walls
  - Pipetting is done less carefully than when calibrating and determining the repeatability
  - The liquid that is pipetted is different from the one that was used for calibrating

In these cases the uncertainty can be **many times higher!**

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## Absorbance

- The physical background for absorbance measurements is very well developed:
- The most important uncertainty sources are:
  - Repeatability of the reading
  - Drift of the photometer parameters during the day
  - Deviation of the photometer reading from the Lambert-Beer law
  - Uncertainty due to the rounding of the last digit

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## Absorbance

- In chemical measurements there can be additional uncertainty contributions:
  - Absorbance increase caused by interfering compounds
  - Uncertainty caused by the influence of interfering compounds on the reaction with the photometric reagent
  - Limited stability of the color of the complex
  - Suspended particles in the solution
- **These effects can be many times larger!**
- **If these effects cannot be eliminated then they have to be taken into account in uncertainty**

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## Sample preparation

- A serious problem for the ISO Method
- Very difficult to model
- Difficult to assign uncertainty contributions in a quantitative way
- The sample preparation uncertainty is usually taken into account by the uncertainty of the **recovery factor  $R$**

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## Uncertainty of $R$ : a possible approach

- Recovery uncertainty is regarded to be composed of three components:
  - $R_m$  the mean method recovery (from eg CRM analysis)
  - $R_s$  correction factor taking into account the differences between the CRM and actual sample
  - $R_{rep}$  correction factor for representativeness (different behaviour of the analyte in spike and real sample)

$$u(R) = R \cdot \sqrt{\left(\frac{u(R_m)}{R_m}\right)^2 + \left(\frac{u(R_s)}{R_s}\right)^2 + \left(\frac{u(R_{rep})}{R_{rep}}\right)^2}$$

Barwick, V. J.; Ellison S. L. R. *Evaluating Uncertainties Associated with Recovery*, VAM Project 3.2.2 Evaluating Confidence in Analytical measurement, part (d), LGC Teddington, 1998

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## What does the result apply to?

- The result can be presented:
  - Only for the laboratory **sample** (sample taken from a large tank, soil sample taken from the field)
  - For the whole **population** (the whole content of the tank, the whole field)
- In the first case the sampling uncertainty is not part of the combined uncertainty
- In the second case **it is!**

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## Prerequisites for successful use of the ISO Method

- **The behaviour of the method must be known sufficiently well, so that an adequate model can be built**
  - The model must be able to take into account all factors that influence the measurement

$$Q_{\text{analyte\_in\_sample}} = \frac{A_{\text{sample}} - b_0}{b_1} \times L \times \frac{1}{R}$$

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## Prerequisites for successful use of the ISO Method

- **The method has to be validated**
  - Confirm that the model is adequate
  - Confirm that the conditions are suitable
- Validation has to be carried out under the same conditions as the use of the method!

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## Prerequisites for successful use of the ISO Method

- **Experiments for determining the uncertainty contributions have to be carried out**
- This has to be done with the same level of care as the actual everyday work, not more carefully!

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## Drawbacks of the ISO Method

- The method gives good results only when all important uncertainty sources have been found and adequately quantified. If not, then the method **tends to give underestimated uncertainties**
- The method has to be thoroughly studied
- This can be quite work-intensive

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## Advantages of the ISO Method

- **The approach is universal and mathematically rigorous**
- **Promotes thinking about the method**
- **Allows to obtain the uncertainty budget**, where it can be seen what are the most important uncertainty contributions and where to invest time and effort
- **The ISO GUM method can be very conveniently combined with establishing traceability of the result**

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## Teaching Uncertainty

- The ISO method **promotes systematic thinking** about all aspects of one's measurement procedure
  - This systematic thinking about the measurement procedure may be more valuable than the actual uncertainty estimate that is obtained
  - We start teaching with the ISO method, but later teach also the Nordtest method

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## Teaching Uncertainty

- The uncertainty concept **has to be introduced at an early stage** of teaching analytical chemistry
  - Uncertainty will be recognised as an intrinsic component of measurement result, not a fancy add/on
  - Especially suitable is to introduce it with the practical classes
  - It can be problematic to find competent teaching staff

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## Teaching Uncertainty

- The importance of the **"chemical" uncertainty sources** has to be stressed
  - Do not limit the teaching to pipettes and balances!
    - In many real situations it happens that these are of minor importance
  - Stress the importance of
    - Sample preparation
    - Interfering compounds
    - Chemical effects (incomplete reaction, fading of color, ...)

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## Teaching MiC at UT

- Teaching MiC
- Teaching of MiC at UT **started in 1999**
  - MiC is now well established in the curricula of chemistry and materials science students
  - The course at present is voluntary, with the commencement of the 3+2 scheme it becomes obligatory

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## Teaching MiC

- There is a dilemma:
  - On one hand:
    - It is desirable to make it clear for the students from the very beginning that Metrological aspects **are an integral part of any measurement**, not just a fancy add-on.
  - On the other hand:
    - Explaining the topics of MiC in full rigor before starting with analytical chemistry has low efficiency, because the concepts of MiC **do not link to anything in the student's knowledge** and will therefore be only partially understood and forgotten very quickly.

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## Teaching MiC at UT: 2 Stages

- **The First stage**
  - The basics of MiC have now been introduced into the general analytical chemistry curriculum
  - Students get:
    - **the very basis** in lectures (measurement, measurement results, their comparability and traceability, measurement uncertainty, the ISO method of uncertainty estimation...)
    - **practical training** in laboratory classes: estimation of measurement uncertainty of real analyses performed by the students

<http://tera.chem.ut.ee/~ivo/akpr1/>  
<http://tera.chem.ut.ee/~ivo/praks/>

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## Teaching MiC at UT: 2 Stages

- **The second stage: Special Course on MiC**
  - In addition to the basics in the general analytical chemistry curriculum there is a **dedicated course on MiC**
  - Topics covered:
    - Metrology, measurement, measurement unit, the SI system, measurement result, measurement uncertainty, comparability and traceability of measurement results, error and uncertainty, estimation of measurement uncertainty, the ISO procedure of uncertainty estimation, other procedures, possible uncertainty sources, uncertainty components, quantifying uncertainty components, metrology in chemistry, method validation, primary methods (gravimetry, titrimetry, coulometry, isotope-dilution mass-spectrometry), reference materials, certified reference materials, interlaboratory comparisons (ILCs), types of ILCs, proficiency testing schemes (PTSS), data treatment of results of PTSS, metrology system in Estonia, the metrology act, metrology in Europe and the World, standards, ISO standards, quality, quality management, quality systems, ISO 17025, accreditation, accreditation in Estonia

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## Teaching MiC at UT

- The “Current Status” of teaching MiC at UT has been published: *Accreditation and Quality Assurance (2002) 7:159-162*

<http://tera.chem.ut.ee/~ivo/metro/>

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