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Grant Agreement No: 860497

GMOS-Train

Global Mercury Observation Training Network in Support of the Minamata Convention

Deliverable D7.6

"Training materials from Summer School 1 on Metrology in Hg measurements"

Start date of project: 01.01.2020 Duration: 60 months

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Acronyms and Abbreviations

PROJECT BENEFICIARIES:

AMU	Université d'Aix-Marseille – Mediterranean Institute of Oceanography, France
CNR IIA	Institute of Atmospheric Pollution Research of the Italian National Research Council, Italy
CNRS	Centre National de Recherche Scientifique, France
HEREON	Helmholtz-Zentrum hereon GmbH, Germany
IFREMER	French Research Institute for Exploitation of the Sea, France
IOS	Institute for Environmental Protection and Sensors, Slovenia
JSI	Jožef Stefan Institute, Slovenia
PSA	PS Analytical, United Kingdom – project exit date 1.7.2020
UGA	Université Grenoble Alpes, France
UPPA	Université de Pau et des Pays de l'Adour, France
SU	Stockholm University, Sweden

PROJECT PARNTER ORGANISATIONS:

AMAP	Arctic Monitoring and Assessment Programme, Norway
AUTH	Aristotle University of Thessaloniki, Greece
EEB	European Environmental Bureau, Belgium
Harvard	Harvard University, USA
IPSJS	International Postgraduate School Jožef Stefan, Slovenia
IRD	Institut de Recherche pour le Développement, France
Lumex	Lumex, Germany/Russia
MIT	Massachusetts Institute of Technology, USA
MSC-E	Meteorological Synthesizing Centre – East of EMEP, Russia
PSA	PS Analytical, United Kingdom – project exit date 1.7.2020
SPRS	Swedish Polar Research Secretariat, Sweden
Tekran	Tekran, Canada
UBL	Université Bretagne Loire , France
UNEP	United Nations Environmental Programme, Switzerland
UPS	Université Paul Sabatier, France
VSL	Dutch National Standard Laboratory, The Netherlands

ESR	Early Stage Researcher
IPR	Intellectual Property Rights

Executive Summary

This document captures the training materials from GMOS-Train Summer School 1 on Metrology in Hg measurements, led by Prof Milena Horvat (JSI) and Dr Igor Živković (JSI). The Summer School was organised as on-line training in basics of metrology concepts and practical examples (29. – 30. 9. 2022), that will be followed by individual ESR projects on uncertainty evaluation which will take place during October – December 2022. Final ESR reports are expected on 22 December, 2022 for completion of the GMOS-Train Deliverable 7.7 "Written reports on uncertainty of Hg measurements from each of the ESRs work". The training course will result in 5 ECTS that will be certified by the GMOS-Train project.

Table of Contents

1. Introduction

According to the Annex 1 of the GMOS-Train Grant Agreement the purpose of the GMOS-Train Summer School 1 "Metrology in mercury measurements" is to address comparability and uncertainty of measurement results. Due to the global Covid-19 pandemic situation, the Summer school 1 has been postponed and organised in two parts:

- Part one: on-line training in basics of metrology concepts and practical examples (29. – 30. 9. 2022).
- Part two: individual ESR projects on uncertainty evaluation which will take place during October – December 2022. It is expected that each ESR will look into the measurements and apply GUM methodology that consists of 4 steps (a tier approach):
  Step 1: Definition of measurand and model for the calculation of uncertainty (10 October, 2022);
  Step 2 and 3: Identification of uncertainty sources and their quantification (7 November, 2022);
  Step 4: Calculation of combined uncertainty (5 December, 2022).

Each ESR will follow the assigned work step-by-step and report to I. Živković and M. Horvat by the dates identified below. Communication will be done with each individual ESR separately with I. Živković and M. Horvat. Final ESR reports are expected on 22 December, 2022 for completion of the GMOS-Train Deliverable 7.7 "Written reports on uncertainty of Hg measurements from each of the ESRs work". This will be a compendium of measurement case studies of the GMOS-Train that be used as a very useful tool for other users as well. Based on the work done we shall prepare a joint technical publication for an appropriate journal, such as Metrologia or similar. All ESR involved will be co-authors of this paper. The Draft joined publication is scheduled for 30 January, 2023.

Presentation of the individual ESR projects on uncertainty evaluation is planned during the project meeting, February 2023 in Hamburg. More detailed instructions will follow. The training course will result in 5 ECTS that will be certified by the GMOS-Train project.

2. Summer School Agenda

GMOS-Train – Metrology training course Programme (PART 1)

29 . – 30. September, 2022

Zoom:
https://us02web.zoom.us/j/85702019608?pwd=bDRSa1U2eFJVVk5uUXF1VzR3eTVYUT09

Day 1, Thursday, 29. September, 2022

9:00 – 9:30	Introduction *(M. Horvat)*
9:30 – 10:30	Basic metrology concepts, approaches, terminology *(Igor Živković)*
	Quiz – questions and answers
10:30 – 11:00	*Coffee break*
11:00 – 12:00	Introduction to measurement uncertainty *(Igor Živković)*
12:00 – 13:00	Uncertainty evaluation in practise
	Practical example 1
13:00 – 14:00	*Lunch break*
14:00 - 15:00	Practical example 2
15:00- 15:30	Quiz – questions and answers

Day 2, Friday, 30. September, 2022

9:00 – 9:45	Traceability and calibration *(Igor Živković, Milena Horvat)*
9:45 - 10:00	Quiz - Questions and answers
10:00 – 11:00	To do and not to do – examples of good practises. (Igor Živković)
11:00 – 11:30	*Coffee break*
11:30 – 12.00	Practical exercises for each individual ESR – assignements (e.g simple case study examples)
14:00 – 15:00	Presentation of the results for each assigned task (ESR presentations)
15:00	Conclusions and closure with instructions for Individual project in Part 2 of the training course

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement no. 860497.

GMOS-Train – Metrology training course
Programme (PART 2)

Work on the individual ESR research projects. Each ESR project will be composed of 4 steps – a tier approach will be used. Each ESR will follow the assigned work step-by-step and report to I. Živković and M. Horvat by the dates identified below. Communication will be done with each individual ESR separately with I. Živković and M. Horvat.

Stepwise approach:

1. Step 1: Definition of measurand and model for the calculation of uncertainty (*10. October, 2022*)
2. Step 2 and 3: Identification of uncertainty sources and their quantification (*7. November, 2022*)
3. Step 4: Calculation of combined uncertainty (5. December, 2022)
4. Final ESR reports (22. December, 2022) for GMOS-Train Deliverable 7.6
5. Draft joined publication (30 January, 2023)
6. Presentation of the individual ESR projects on uncertainty evaluation during the project meeting, February 2023. Instructions will follow.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement no. 860497.

3. Training material

3.1 Introduction

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement no. 860497.

Metrology in mercury measurements

dr. Igor Živković
prof. dr. Milena Horvat

Virtual event
29-30 September, 2022

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement no. 860497.

Agenda

1 Introduction

2 Basic metrology concepts, approaches, terminology

3 Introduction to measurement uncertainty

4 Practical Example 1

5 Practical Example 2

6 Traceability and calibration

7 To do / not to do

8 Practical exercises for each individual ESR

1 Introduction

Aims

- What you will learn?
    - To apply metrological approaches in analytical work in mercury analysis and speciation for the estimation of measurement uncertainty
    - To understand the meaning of basic concepts, approaches, and terminology in metrology
    - To determine each ESR's measurement uncertainy of their respective methods
    - To obtain a knoledge of determining uncertinaty components and calculate expanded uncertainty
    - To learn how to properly report the measurement result
    - To learn how to properly report Hg speciation data
    - Traceability and calibration

Thinking in analytical chemistry

Traditional

- My result is correct, but I don't need to show why
- It is not necessary to state & demonstrate traceability
- It is not possible to write model equation
- It is not possible to use a common approach for uncertainty estimation
- The smaller the number behind " ± " the better my laboratory
- I did this for long time and I know my business

Metrological

- Limited information: 'the Truth' only exists theoretically, as it can only be approximated
- Realism: just do what you can, it will never be perfect
- Transparency: document in an open way, leaving nothing out
- Critical review: there are never problems, unless you look critically
- Standardised/unified language and practices across disciplines & sectors

Chemical metrology

- Metrology

= science of measurements

= understanding measurement procedures

Sampling	+	Processing	+	Measurement	=	Result
Representative Appropriate Contamination Stability Handling		Dissolution Extraction Dilution		Comparison to SI units or conventional scale		± uncertainty

Sampling uncertainty

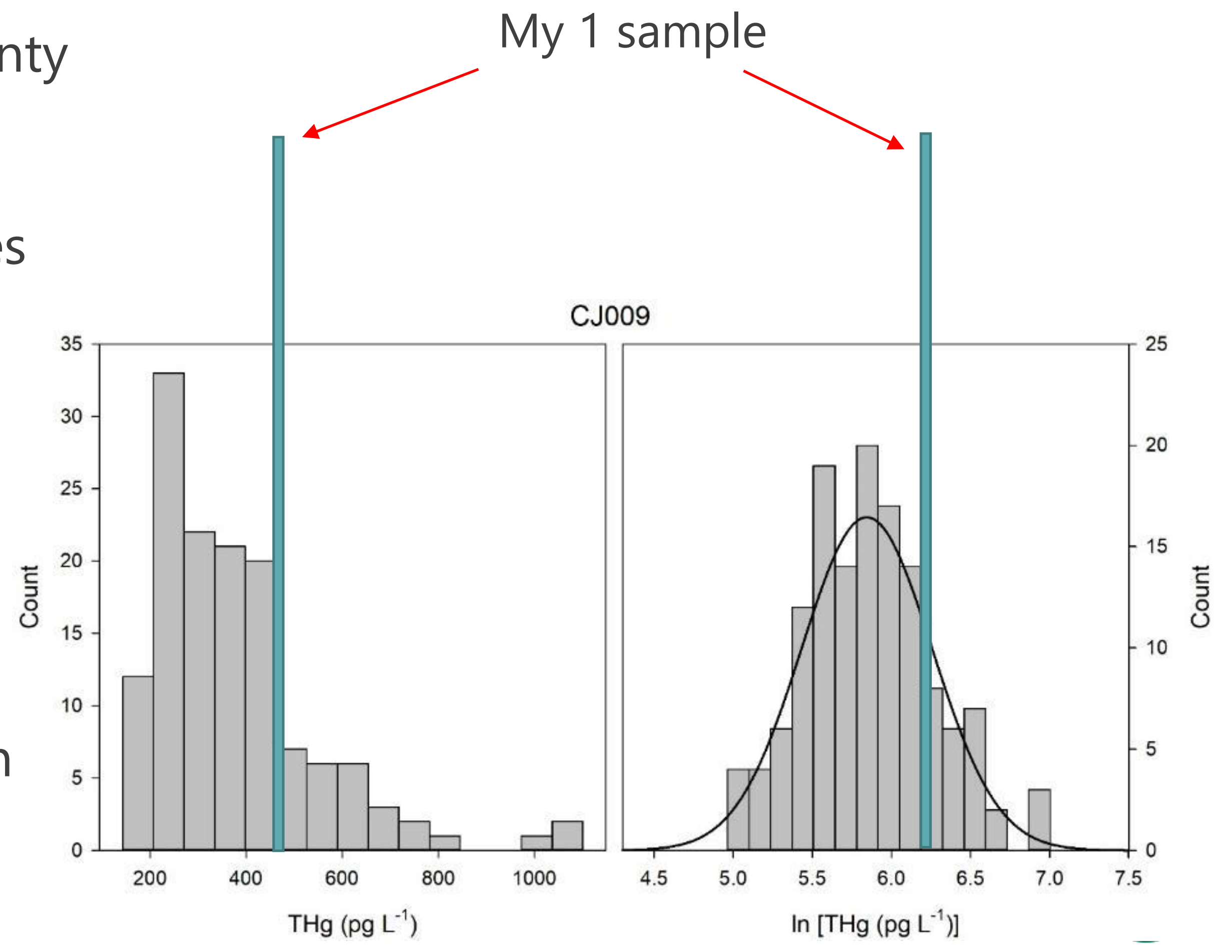
Sampling	+	Processing	+	Measurement	=	Result
Representative Appropriate Contamination Stability Handling		Dissolution Extraction Dilution		Comparison to SI units or conventional scale		± uncertainty

- Sampling uncertainty vs. measurement uncertainty

- <u>Representative and appropriate sample</u>
    - Hardly achievable for environmental samples
    - Influence of environmental Hg transport
    - Changes in anthropogenic loads
    - Transformations of Hg species

- My 1 sample is not representative

- Distribution of THg data at one sampling station
    - Normal or log-normal scale

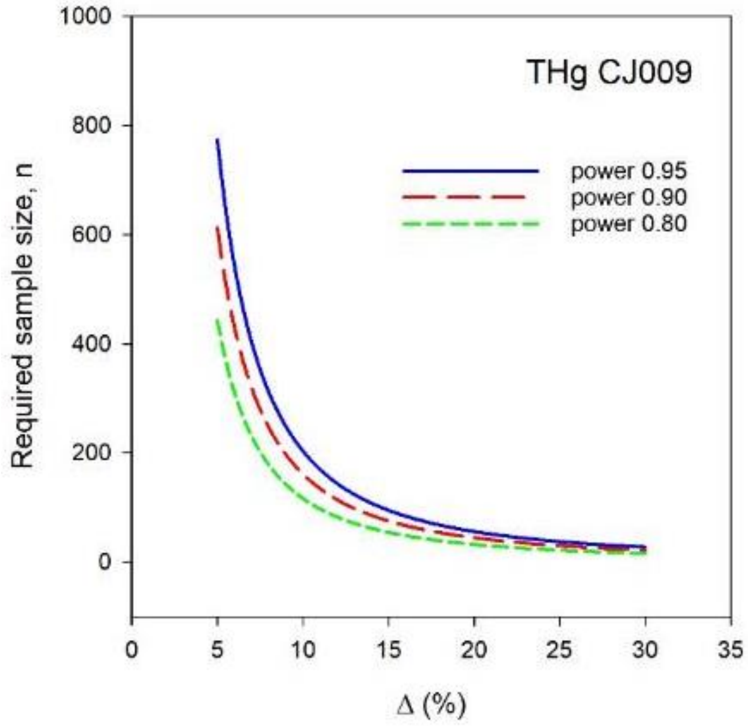


Sampling uncertainty

Sampling	+	Processing	+	Measurement	=	Result
Representative Appropriate Contamination Stability Handling		Dissolution Extraction Dilution		Comparison to SI units or conventional scale		± uncertainty

- How many samples do we need to observe a difference between samples?
  - Short answer – A lot

  - Depends on how sure we want to be that the difference actually exists
  - Statistical power



- Sample contamination
  - Reagents (appropriate acid for preservation for various samples)
  - Sampling equipment (Niskin bottle, clean bottles, denuder, traps…)

Sampling uncertainty

Sampling	+	Processing	+	Measurement	=	Result
Representative Appropriate Contamination Stability Handling		Dissolution Extraction Dilution		Comparison to SI units or conventional scale		± uncertainty

- Stability
  - When to analyse: DGM, THg, DMeHg?
  - On board or laboratory?
  - What we can preserve (acidify)?
  - Speciation issues!
- Handling
  - Fridge or freezer?
  - Thawing/re-freezing?
  - Transportation of sample?
- Sample contamination
  - Reagents (e.g., appropriate acid for preservation for various samples)
  - Sampling equipment (clean Niskin bottle, clean bottles, denuder, traps…)

Sampling	+	Processing	+	Measurement	=	Result
Representative Appropriate Contamination Stability Handling		Dissolution Extraction Dilution		Comparison to SI units or conventional scale		± uncertainty

Sample processing

- Processing
  - How – depends on
    - Sample type
    - What is our analyte
  - Solids – acid digestion, pyrolysis, extraction for MMHg…
  - Liquids – **BrCl digestion**, dichloromethane extraction, **direct hydride generation**…
  - Gaseous – carbon traps, gold traps, denuders for Hg(II)…

Practical Example 1

Practical Example 2

- Every step contributes to the procedural blanks and consequently to measurement uncertainty!

Measurement

Sampling +	Processing +	Measurement =	Result
Representative Appropriate Contamination Stability Handling	Dissolution Extraction Dilution	Comparison to SI units or conventional scale	± uncertainty

- What is a measurement?
- Any measurement is the establishment of a <u>ratio</u> of an unknown number to a known number, defining the agreed unit and provided that the numerator and the denominator are expressed in the same unit (de Bievre, 1998).

- e.g., determination of MeHg in seawater by hydride generation

$$c(MeHg) = \frac{A\,(S)}{A\,(Std)} * n(Std) * \frac{1}{V(S)}$$

Ratio of peak area of sample (unknown) to a peak area od standard solution (known)

The amount of MeHg in our sample (pmol)

MeHg concentration in our sample (pmol/L)

Measurement

Sampling	+	Processing	+	Measurement	=	Result
Representative Appropriate Contamination Stability Handling		Dissolution Extraction Dilution		Comparison to SI units or conventional scale		± uncertainty

- What is a result?

- In general, the result of a measurement is only an approximation or estimate of the value of the measurand and thus is complete only when accompanied by a statement of the uncertainty of that estimate (BIPM, 2008)

- Result has to be accompanied by corresponding measurement uncertainty

Result ± uncertainty (unit)

- Analytical measurements need to be comparable in time and space
- Traceability is the best way to achieve this

3.2 Basic metrology concepts, approaches, terminology + Quiz

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement no. 860497.

2 Basic metrology concepts, approaches, terminology

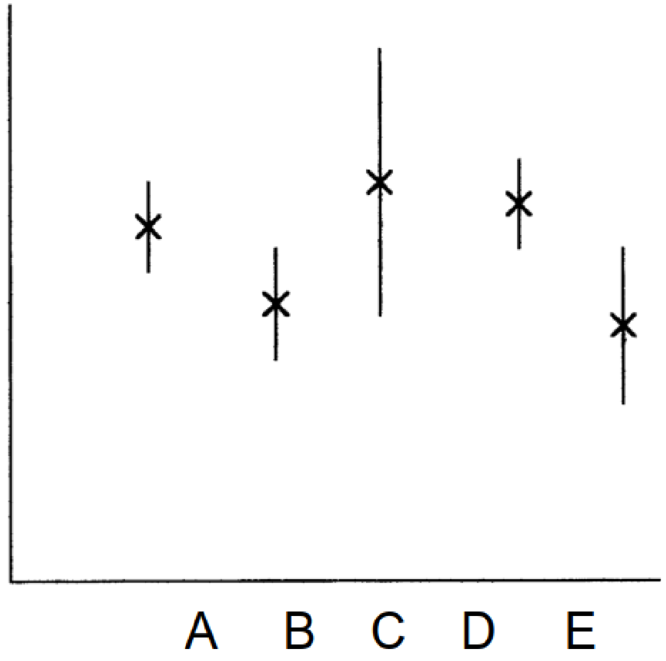
Measurement

- The objective of a **measurement** is to determine the value of the **measurand** that is, the value of the **particular quantity** to be measured. A measurement therefore begins with an appropriate specification of the measurand, the **method of measurement**, and the **measurement procedure** (BIPM, 2008).

- Example:
- Analyte: methylmercury (MeHg)
- Measurand: the concentration of methylmercury in seawater
- Particular quantity: MeHg concentration in seawater in pmol/L
- Method of measurement: Cold vapor atomic fluorescence spectrometry
- Measurement procedure: SOP for the determination of MeHg concentration in seawater by hydride generation

Measurement 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
- It is fundamental property of a result
- Uncertainty is NOT an error
- Required for the standard SIST EN ISO/IEC 17025
- Used for:
- Assessment of the reliability of the result
- Confidence that can be placed in any decisions based on its use
- Comparison of measurement results



Measurement uncertainty

Measurand……..concentration of an analyte

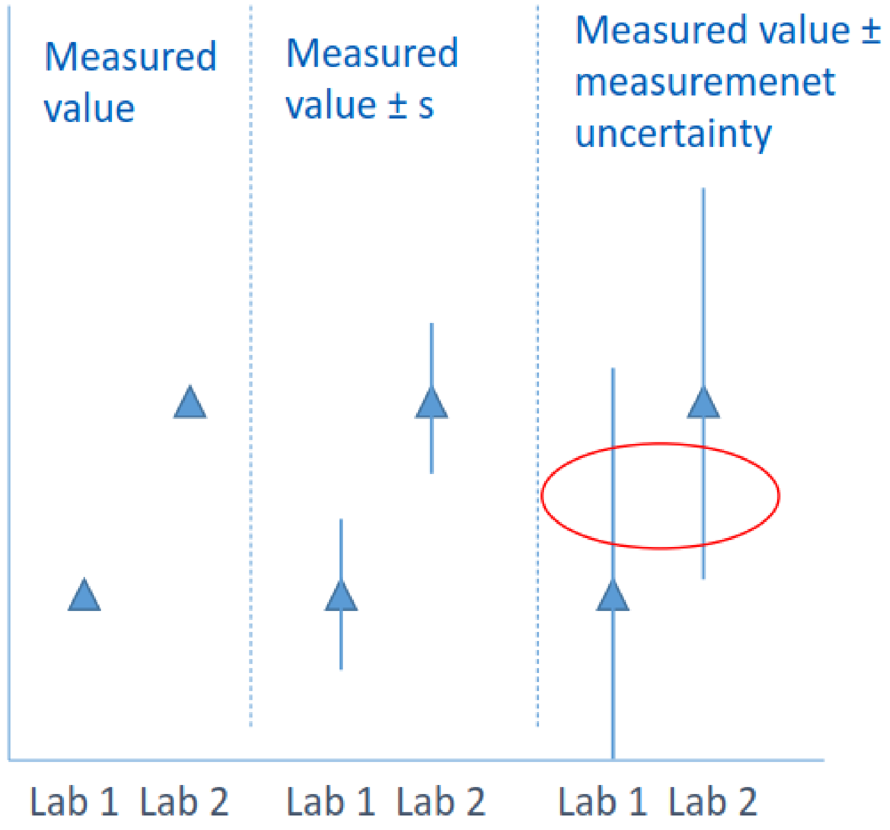
- The parameter may be, for example, a standard deviation (or a given multiple of it), or the width of a confidence interval

- Uncertainty of measurement comprises, in general, many components: Type A and Type B estimations

Measurement uncertainty

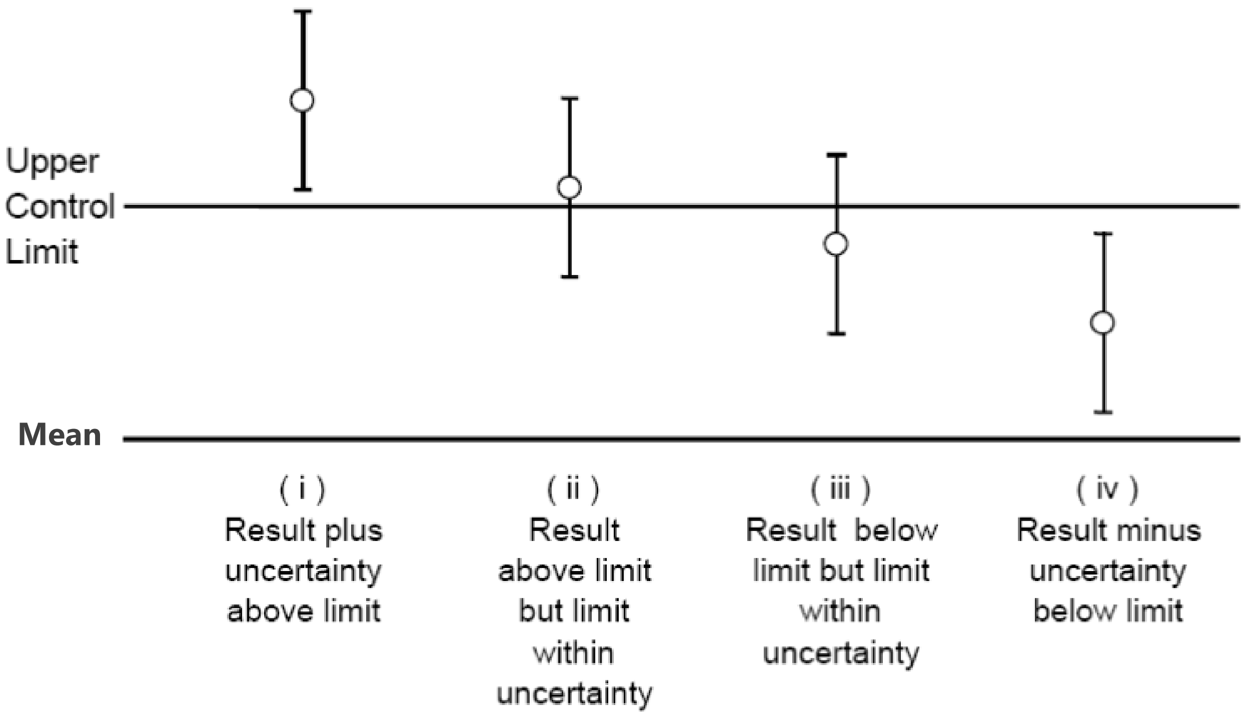
- Result of a measurement itself is an <u>estimation</u> of a true value

- to assess the reliability of the result
- to know the confidence that can be placed in any decisions based on its use
- in order to compare measurement results



Measurement uncertainty

- Compliance against limits
- (Eurachem)



Measurement uncertainty – Definitions (BIPM, 2008)

Standard uncertainty: uncertainty of the result of a measurement expressed as a **standard deviation**

Type A evaluation (of uncertainty): method of evaluation of uncertainty by the statistical analysis of series of observations

Type B evaluation (of uncertainty): method of evaluation of uncertainty by means other than the statistical analysis of series of observations

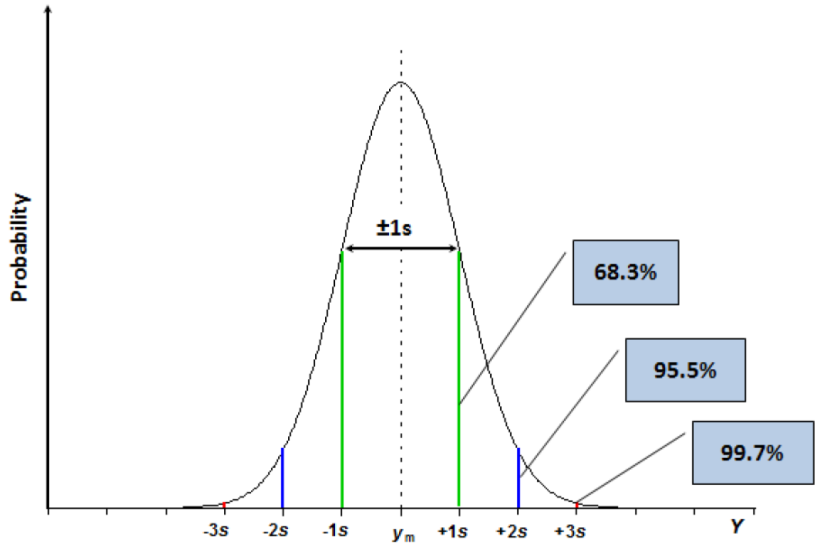
Combined standard uncertainty: standard uncertainty of the result of a measurement when that result is obtained from the values of a number of other quantities [...]

Expanded uncertainty: quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand

Coverage factor: numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty

Standard deviation and normal distribution

- Normal (Gauss) distribution



- Many distribution functions known to mathematicians and many of them are encountered in the nature, i.e., they describe certain processes in the nature

- The importance of the normal distribution stems from the Central limit theorem

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$$

σ – standard deviation
x – individual result
μ – mean of individual results

Standard deviation and normal distribution

Population

VS

Sample

N – number of samples

s_N – population standard deviation

N = ∞

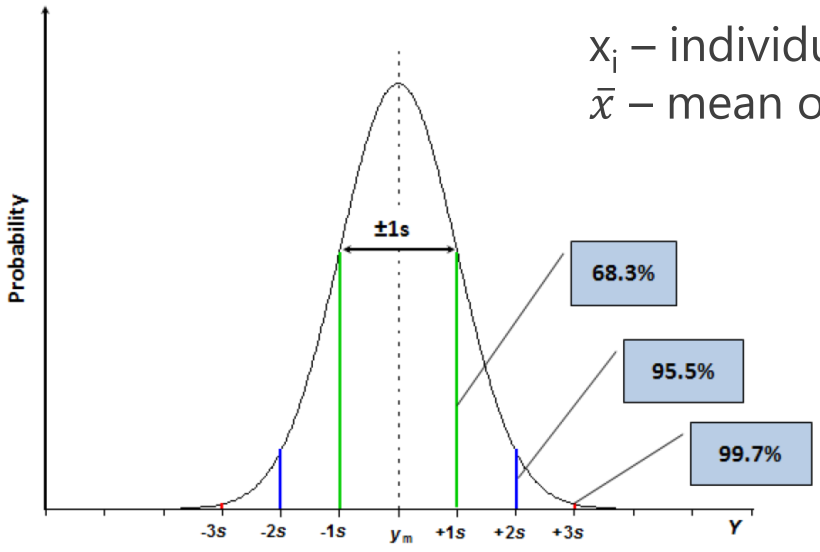
s – sample standard deviation

N = small number

- Standard deviation

- Population $$s_N = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \bar{x})^2},$$

- Sample $$s = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \bar{x})^2}.$$



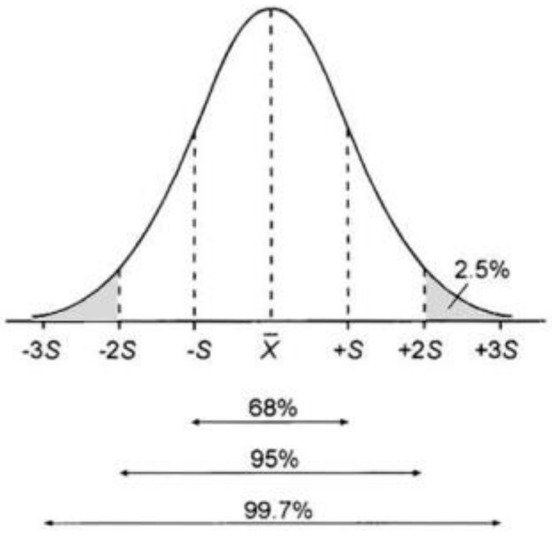
x_i – individual result

$\bar{x}$ – mean of individual results

If a measurement result is simultaneously influenced by many uncertainty sources and if the number of the uncertainty sources approaches infinity then the distribution function of the measurement result approaches the normal distribution, irrespective of what are the distribution functions of the factors/parameters describing the uncertainty sources (BIPM, 2008).

Standard deviation and normal distribution

$$s = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{n-1}}$$



- Normal (Gauss) distribution

$$u(x_i) \equiv s$$

- Eksperimental data
- Standard deviation (quantitative estimation of the range of measured values)
- Used to define confidence interval (a range of estimates for an unknown parameter)
- For SD, a large (infinite) number of measurements needed
- Practically, an approximate standard deviation is calculated for N = 6 – 10

- What if we have only 2 measurements? Or only 1? (Chapter 7)

	6.06
	6.71
	5.23
	6.00
	5.78
	6.59
	5.23
	5.88
	6.22
	6.02
	6.41
	6.36
	6.42
	6.47
	6.05
	6.05
	6.49
	7.00
average	5.86
stdev	0.42

Types of evaluation of uncertainty

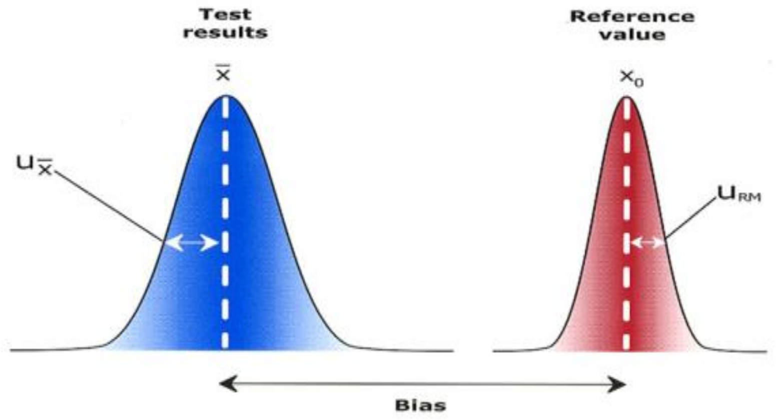
- Type A
- Experimental data - large number of measurements
- Estimated from the statistical distribution of the results of series of measurements and can be characterised by <u>standard deviations</u>

- Type B
- Estimated from assumed probability distributions **based on experience** or other information (e.g. producer's data, calibration certificates…)
- Characterised by standard deviations as well:
  - <u>rectangular distribution</u>
  - <u>triangular distribution</u>

Precision, accuracy, trueness

- Precision is the measure of the degree of repeatability of an analytical method under normal operation
- Precision shows how close results are to one another

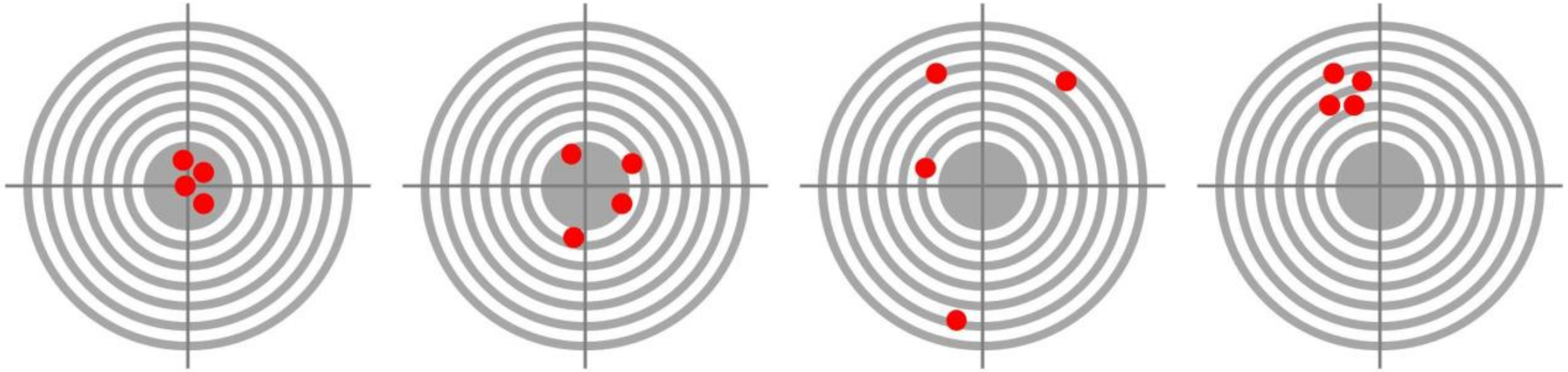
- Trueness is the closeness of agreement between the average of an <u>infinite number</u> of replicate measured quantity values and a <u>reference quantity value</u>
- Bias is a quantitative expression of trueness (trueness of result improves when bias decreases)
- Bias can be only estimated



- (VIM)

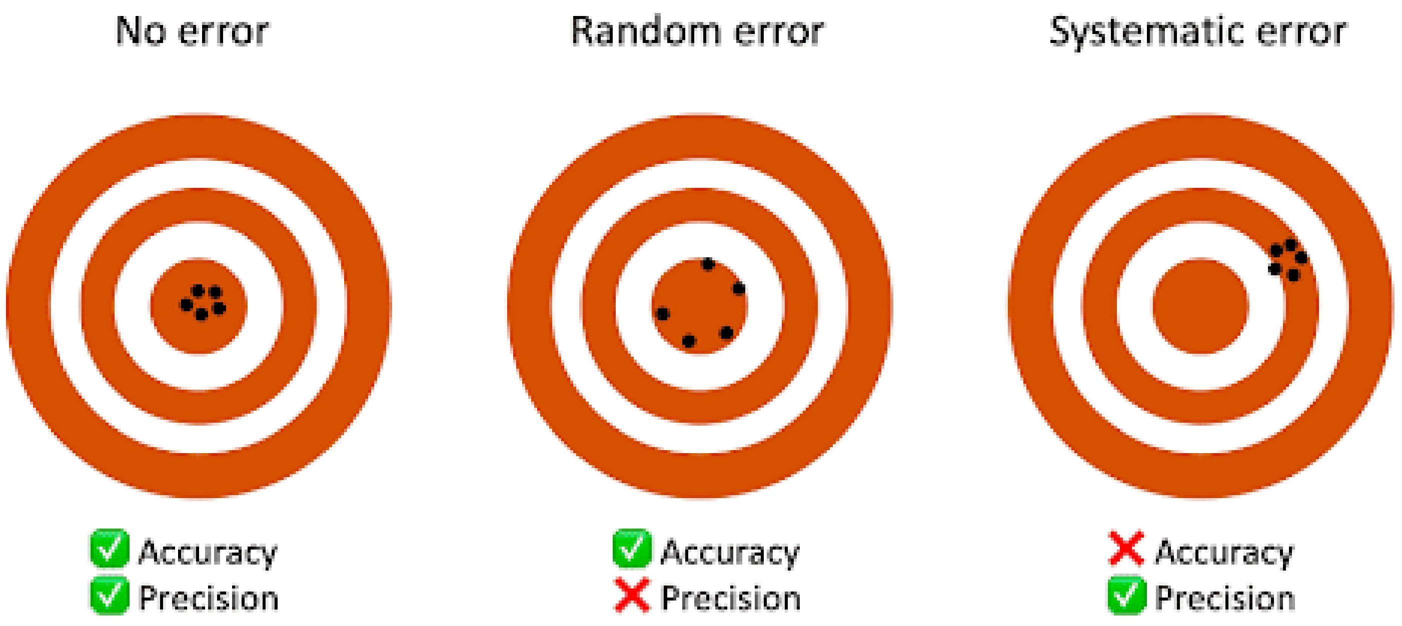
Precision, accuracy, trueness

- Accuracy is the closeness of agreement between a measured quantity value and a „true" quantity value of a measurand
- Describes the measure of exactness of an analytical method
- Trueness applies to the average value of a large number of measurement results
- Accuracy applies to a single result of measurement.
- CRM
- (VIM)



High accuracy, good precision, good trueness | Low accuracy, poor precision, good trueness | Low accuracy, low precision, poor trueness | Low accuracy, high precision, poor trueness

Error



Random error source

- **Natural variations**
- **Imprecise instrument**
- **Individual differences**

Sources of systematic errors

- **Response bias**
- **Instrumental drift**
- **Sampling bias**

Q&A

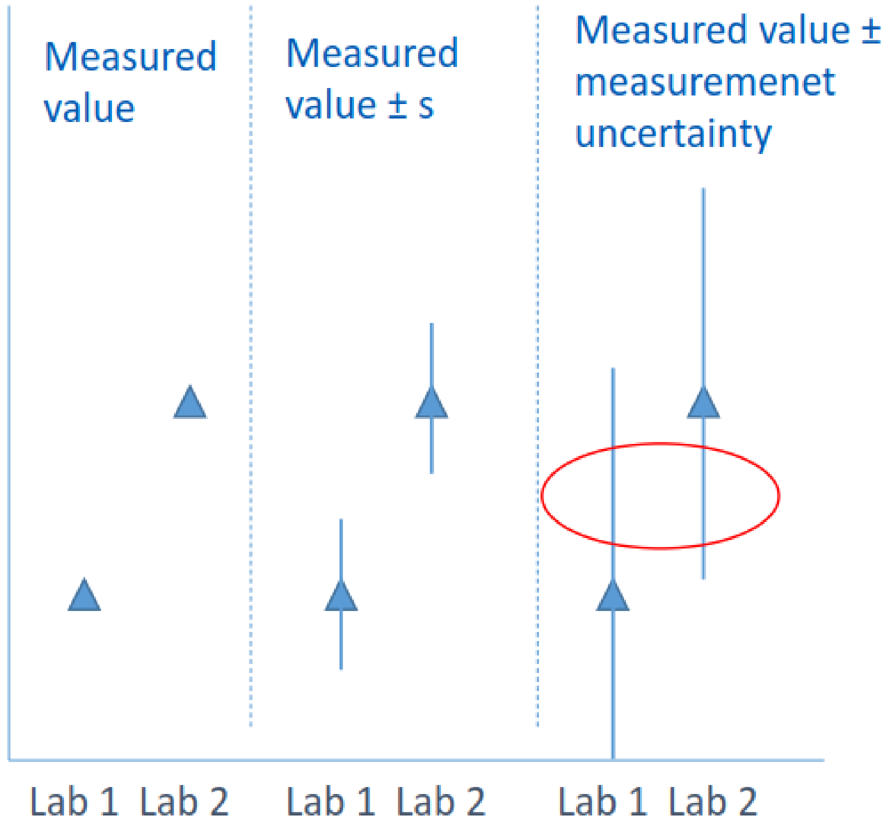
Measurement

- Analyte? Se in blood THg DGM
- Measurand? mol of Zn in water pg of THg %MeHg Length of day mL of acetone
- Method of measurement? CVAAS ICP-MS Ruler, watch

Volume

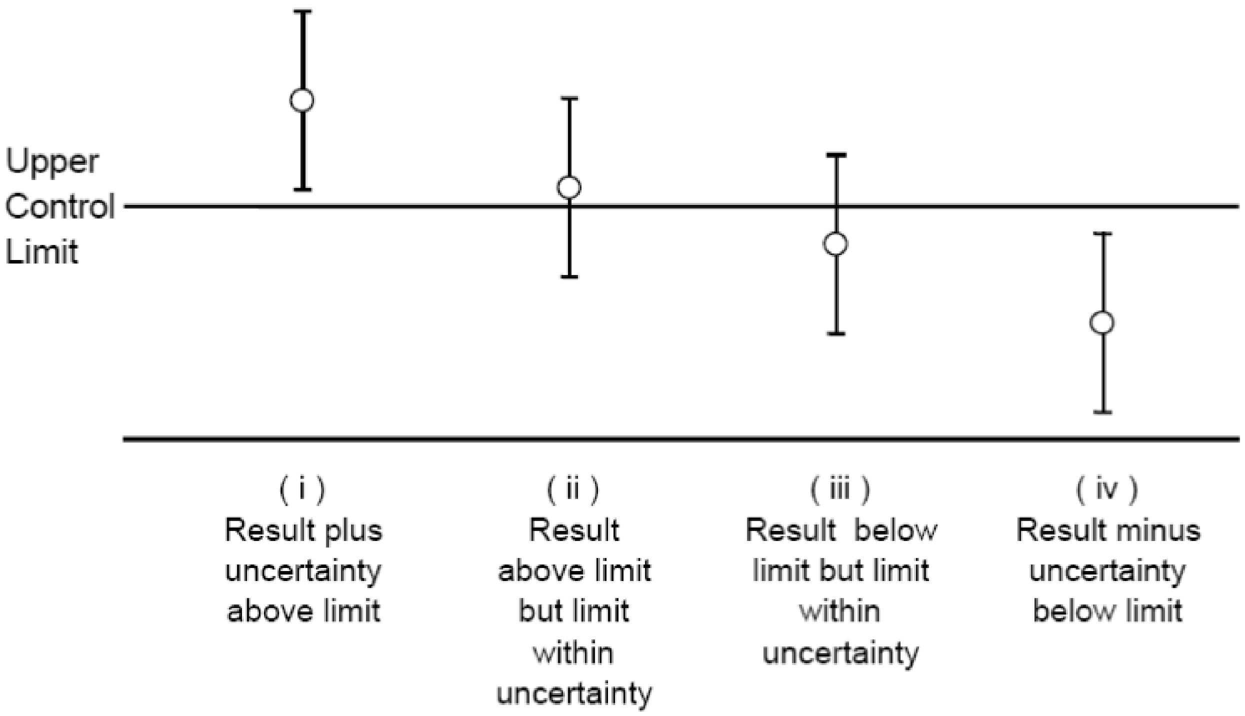
Measurement uncertainty

- Is there a difference between Lab 1 and Lab 2?
- Why?



Measurement uncertainty

- Which data are good?



Standard deviation and normal distribution

- Calculate standard deviation
- Manually, not using =stdev() function

$$s = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{n-1}}$$

	5.47
	5.66
	4.97
	5.34
	5.08
	5.13
	5.37
	5.40
	4.96

Types of evaluation of uncertainty

- Type A
- Experimental data - large number of measurements

- Type B
- Estimated from assumed probability distributions based on experience or other information (e.g. producer's data, calibration certificates...)

5.47
5.66
4.97
5.34
5.08
5.13
5.37
5.40
4.96

Certificate of Analysis

Standard Reference Material® 3133

Mercury (Hg) Standard Solution

Lot No. 061204

This Standard Reference Material (SRM) is intended for use as a primary calibration standard for the quantitative determination of mercury. The mass fraction of mercury is certified. For added benefit to the user, information values for the isotopic composition of mercury are also provided. A unit of SRM 3133 consists of five 10 mL sealed borosilicate glass ampoules of an acidified aqueous solution prepared gravimetrically to contain a known mass fraction of mercury. The solution contains nitric acid at a volume fraction of approximately 10 %.

Certified Value of Mercury: 9.954 mg/g ± 0.053 mg/g

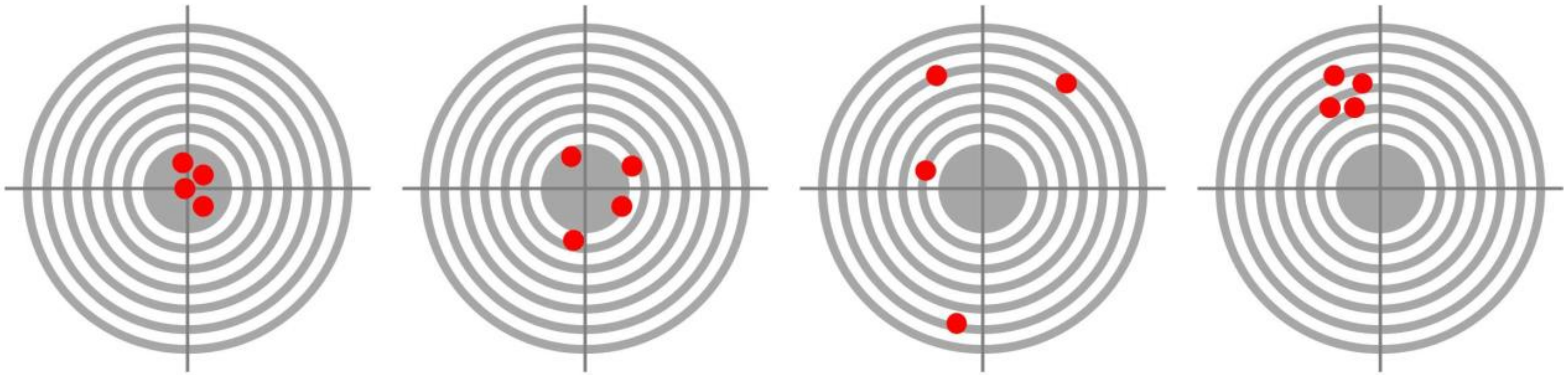
Precision, accuracy, trueness

- Trueness is the closeness of agreement between the average of an **infinite number** of replicate measured quantity values and a reference quantity value
- Bias is a quantitative expression of trueness (trueness of result improves when bias decreases)

- Q: Can we ever know the bias of our measurement method?
- Q: Why?

Precision, accuracy, trueness

- Which one is the second best case?



High accuracy, good precision, good trueness

Low accuracy, poor precision, good trueness

Low accuracy, low precision, poor trueness

Low accuracy, high precision, poor trueness

3.3 Introduction to measurement uncertainty

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3 Introduction to measurement uncertainty

Different approaches to measurement uncertainty

Two approaches to the determination of the measurement uncertainty

- 1st approach – Nordtest approach
- „Shortcut" approach

- Takes only into an account results from measurements of certified reference materials (CRM)
- Only possible when reference material exists
- This approach assumes that data variability in CRM results corresponds to similar variability in sample results – sample matrix must match with CRM
- Single-laboratory validation approach
- Not recommended as it considers only bias

2nd approach – ISO-GUM approach

- Bottom-up approach
- Every step of your work is known

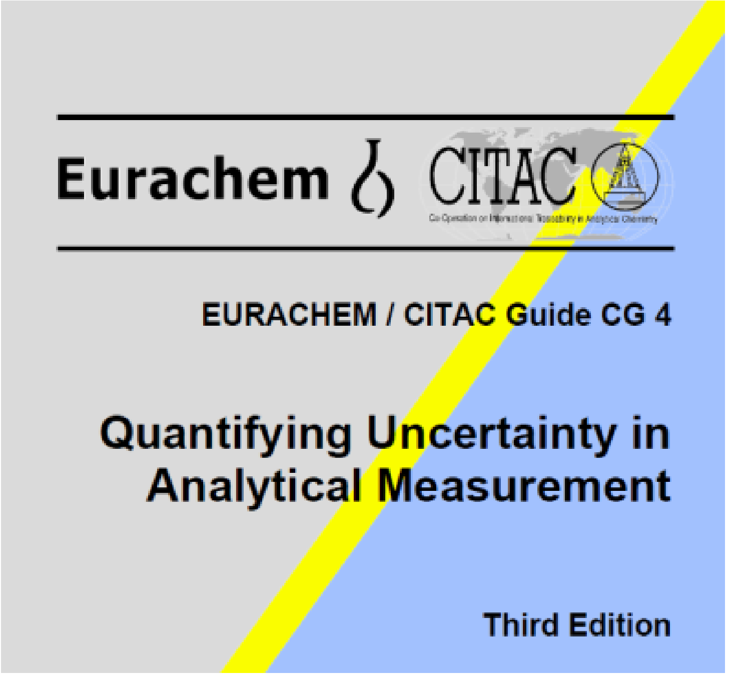
General strategy

- Guide to the expression of uncertainty in measurement

- Model equation (EURACHEM Guide)

- Monte Carlo Simulation

- Uncertainty estimation based on standard deviations: repeatability and reproducibility of the measurement results (validation data, QA/QC data, inter-lab comparisons)



2nd approach – ISO-GUM approach

- Benefits of Monte Carlo
- Exact distribution
- https://uncertainty.nist.gov/

1. Select Inputs & Choose Distributions

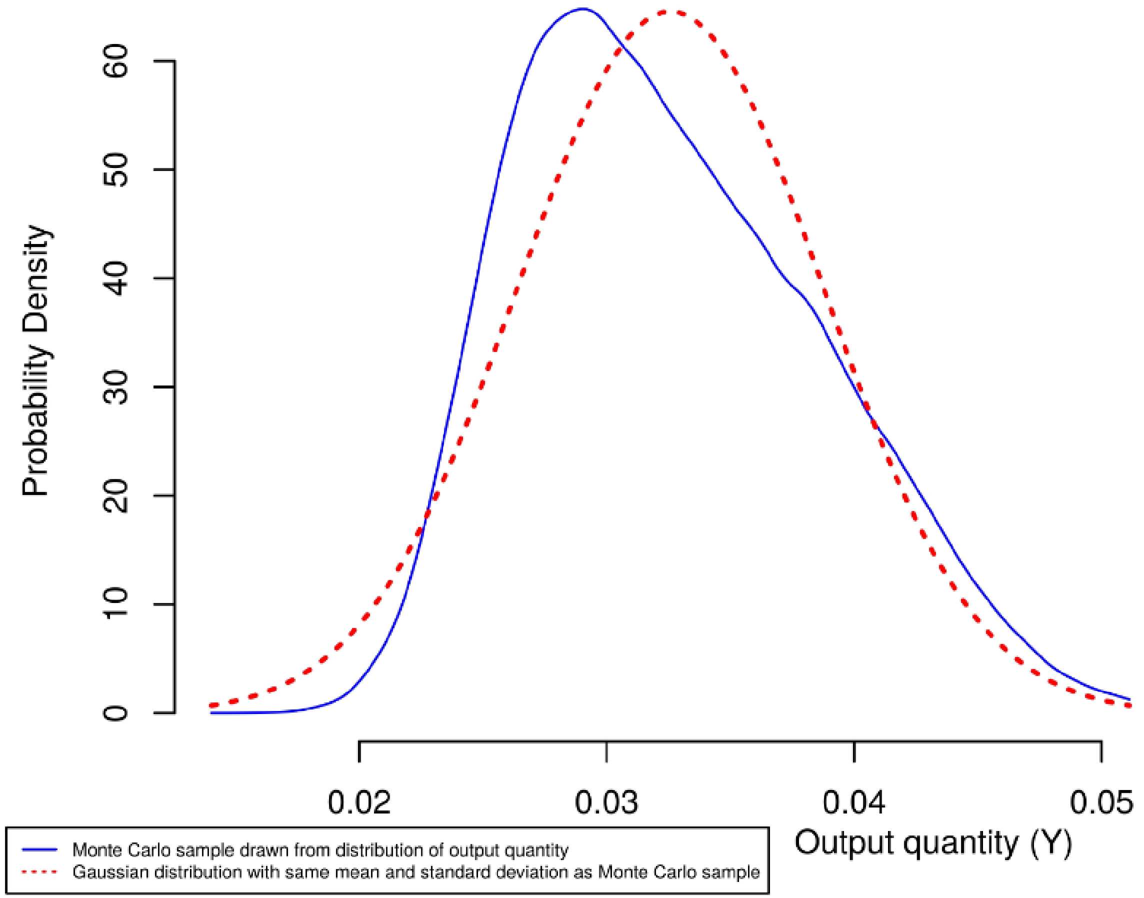
Number of input quantities: 2

Names of input quantities:

m	V

m	Gaussian (Mean, StdDev)	10	1
V	Rectangular (Left Endpoint, Right Endpoint)	230	400

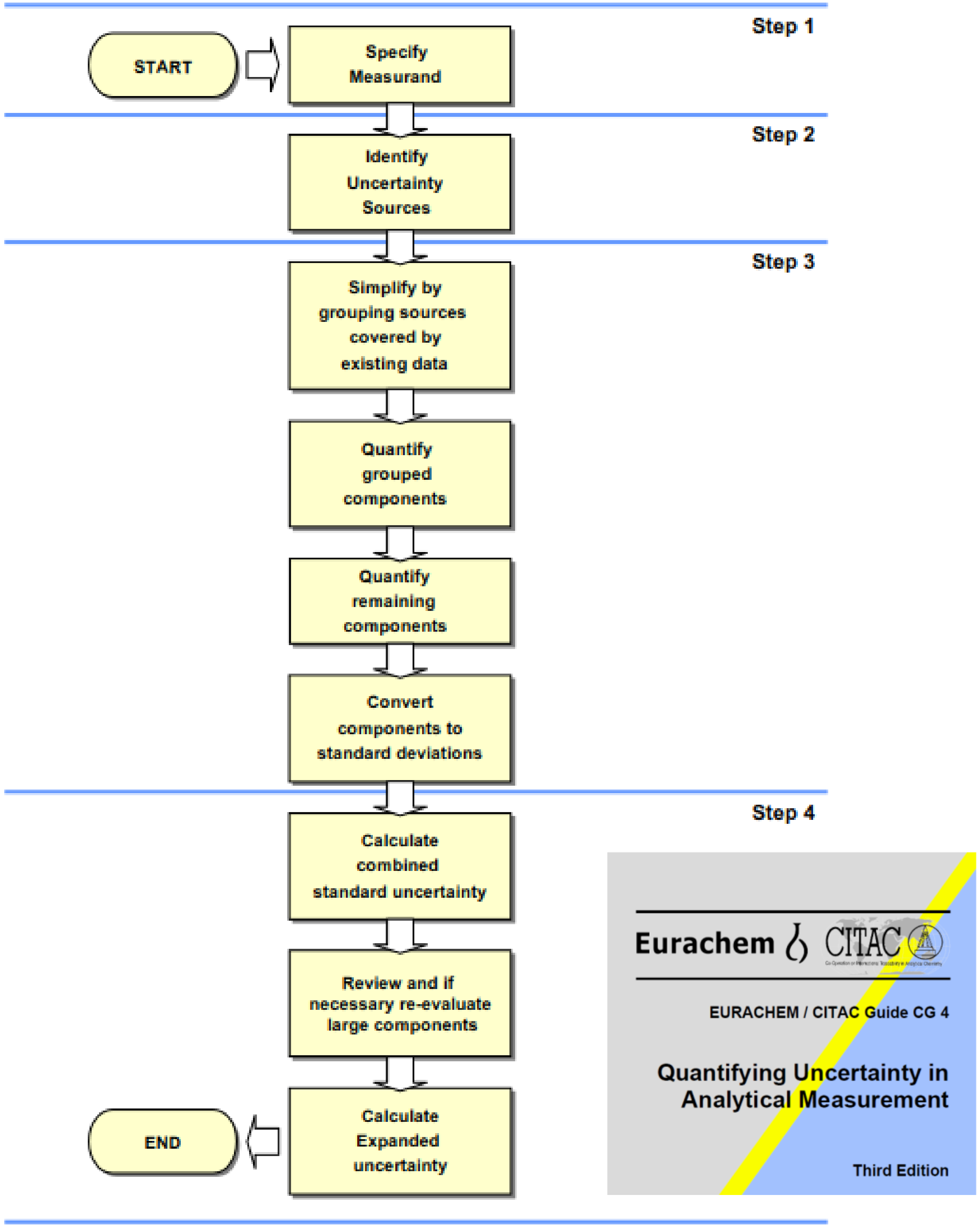
Correlations



ISO-GUM approach

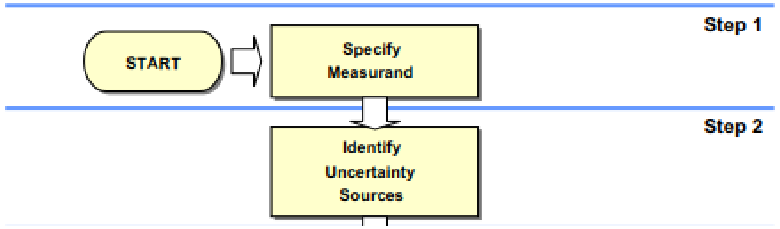
- Step 1: Specify Measurand
- Step 2: Identify Uncertainty Sources
- Step 3: Quantify Uncertainty Components
- Step 4: Calculate Combined Uncertainty

- <u>Working Example 0: Density of solution</u>
    - (because it is simple)



ISO-GUM approach – Step 1: Specify Measurand

- In most cases, a measurand Y is not measured directly, but is determined from N other quantities $X_1, X_2, \ldots, X_N$ through a functional relationship *f* (model equation):

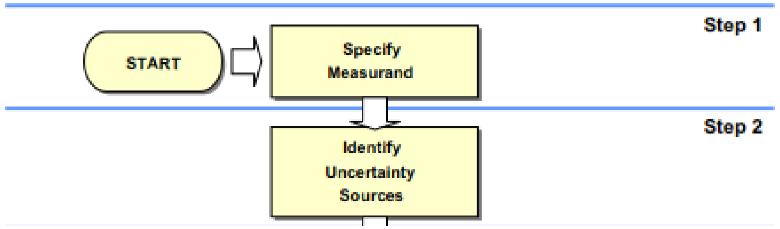


- $Y = f(X_1, X_2, \ldots, X_N)$
- Density ρ = *f* (mass **m**, volume **V**)

- The same symbol (Y) is used for the physical quantity (the measurand) and for the random variable that represents the possible outcome of an observation of that quantity
- The estimate of X_i (strictly speaking, of its expectation) is denoted by x_i (m of 525 g, V of 500 mL).

- The input quantities $X_1, X_2, \ldots, X_N$ upon which the output quantity Y depends may themselves be viewed as measurands and may themselves depend on other quantities

ISO-GUM approach – Step 1: Specify Measurand



- If data indicate that *f* does not model the measurement to the degree imposed by the required accuracy of the measurement result, additional input quantities must be included in *f* to eliminate the inadequacy (e.g., recovery, reproducibility…) (Eurachem guide)

- An estimate of the measurand Y, denoted by y, is obtained from input estimates x_1, x_2, …, x_N for the values of the N quantities X_1, X_2, …, X_N.

- The output estimate y, which is the result of the measurement, is given by:

- $y = f(x_1, x_2, \ldots, x_N)$
- $\rho = f\,(m, V)$

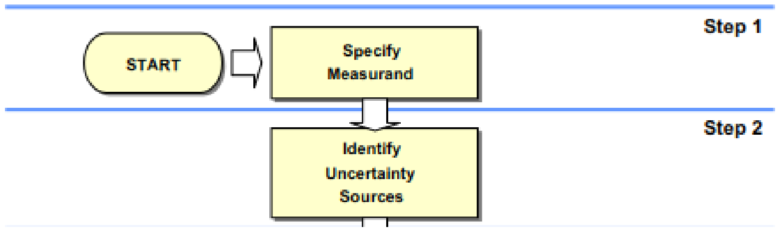
ISO-GUM approach – Step 1: Specify Measurand

- A clear statement of what is being measured, including the relationship between the measurand and the parameters (e.g. measured quantities, constants, calibration standards, etc.)
- Quantitative expression (**model equation**) relating the value of the measurand to the parameters on which it depends
- Example: density of the green solution

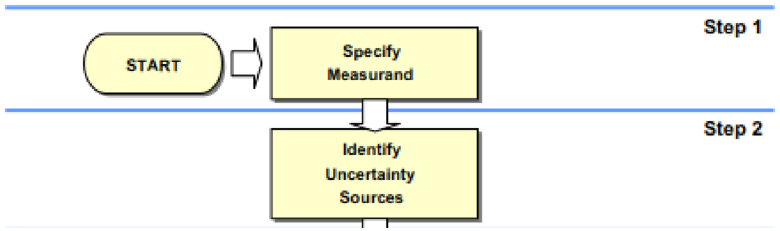
$$\rho(green\ solution) = \frac{m(green\ solution)}{V(green\ solution)}$$

measurand

analyte



ISO-GUM approach – Step 2: Identify Uncertainty Sources



- Eurachem:
- „List the possible sources of uncertainty. This will include sources that contribute to the uncertainty on the parameters in the relationship specified in Step 1, but may include other sources and must include sources arising from chemical assumptions (e.g. recovery)."

$$\rho(green\ solution) = \frac{m(green\ solution)}{V(green\ solution)} * F_{rep}$$

1 by definition, but has uncertainty

- <u>Not all researchers include additional sources, thus artificially decreasing their uncertainy!</u>

ISO-GUM approach – Step 2: Identify Uncertainty Sources

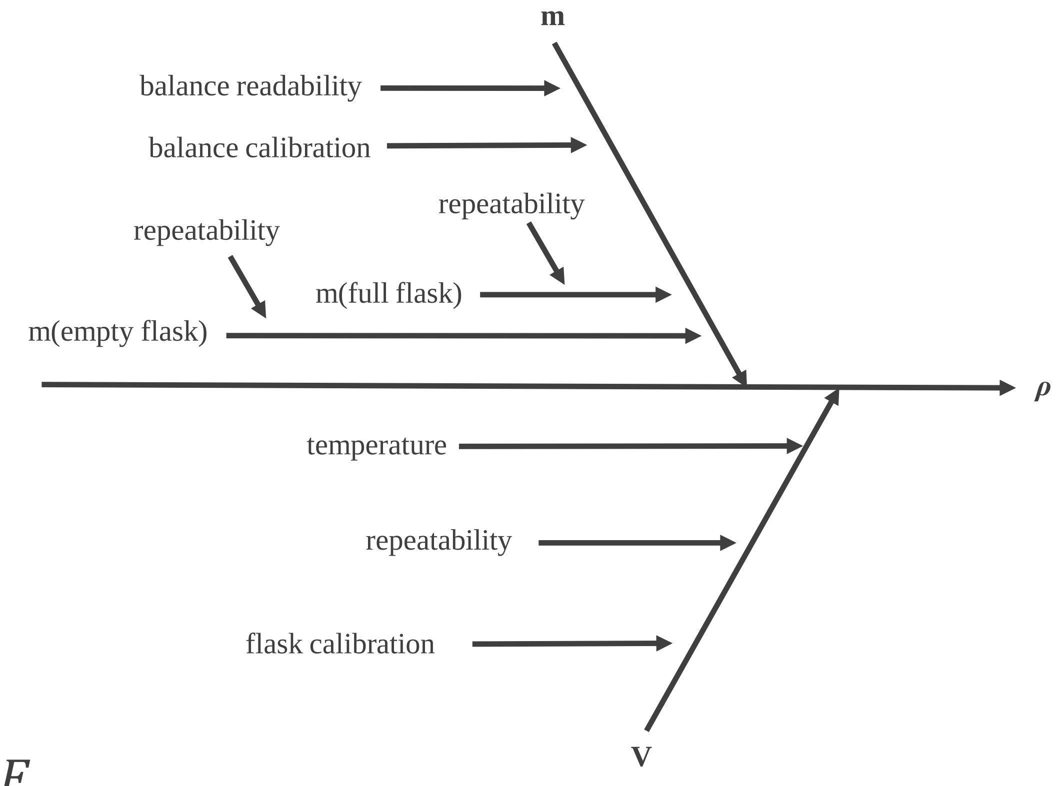
BIPM: In practice, there are many possible sources of uncertainty in a measurement, including:

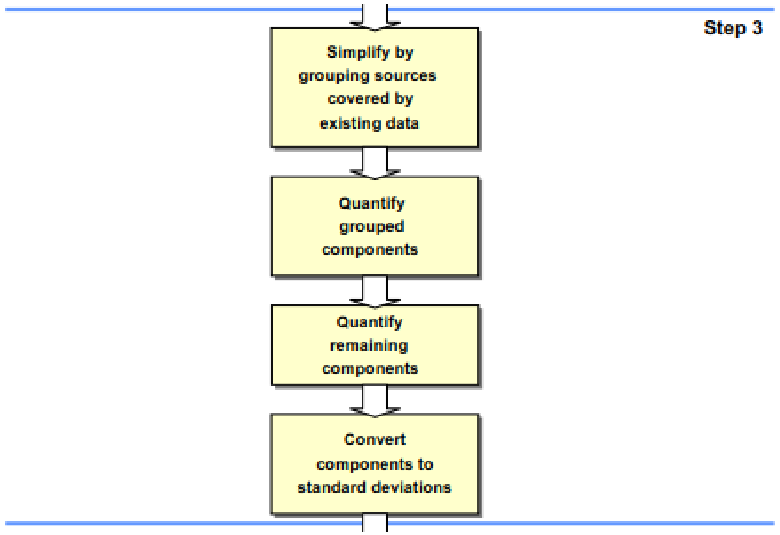
- a) incomplete definition of the measurand;
- b) imperfect realization of the definition of the measurand;
- c) nonrepresentative sampling — the sample measured may not represent the defined measurand;
- d) inadequate knowledge of the effects of environmental conditions on the measurement or imperfect measurement of environmental conditions;
- e) personal bias in reading analogue instruments;
- f) finite instrument resolution or discrimination threshold;
- g) inexact values of measurement standards and reference materials;
- h) inexact values of constants and other parameters obtained from external sources and used in the data-reduction algorithm;
- i) approximations and assumptions incorporated in the measurement method and procedure;
- j) variations in repeated observations of the measurand under apparently identical conditions.

ISO-GUM approach – Step 3: Quantify Uncertainty Components

- Start with the basic expression used to calculate the measurand from intermediate values
- The cause and effect diagram – fishbone (Ishikawa) diagram

$$\rho = \frac{m}{V} * F_{rep}$$





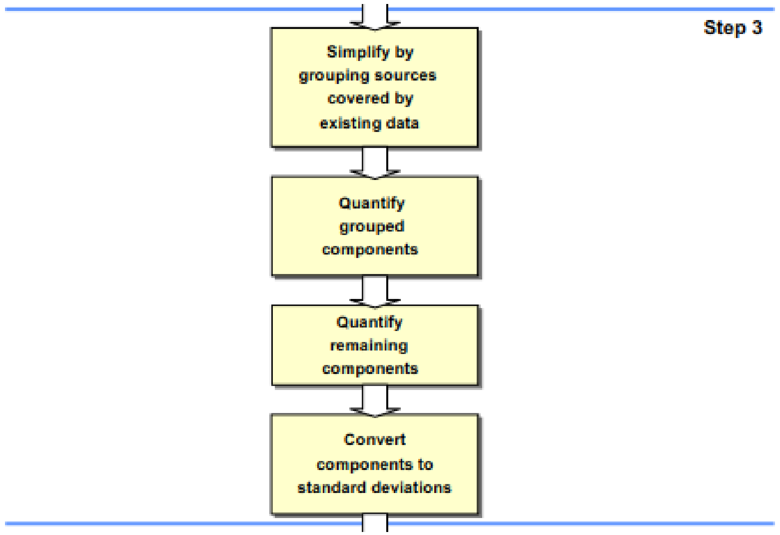
$$\rho = \frac{m(full) - m(empty)}{V} * F_{rep}$$

ISO-GUM approach – Step 3: Quantify Uncertainty Components

Estimate standard uncertainties (how?) of each member of fishbone diagram using:

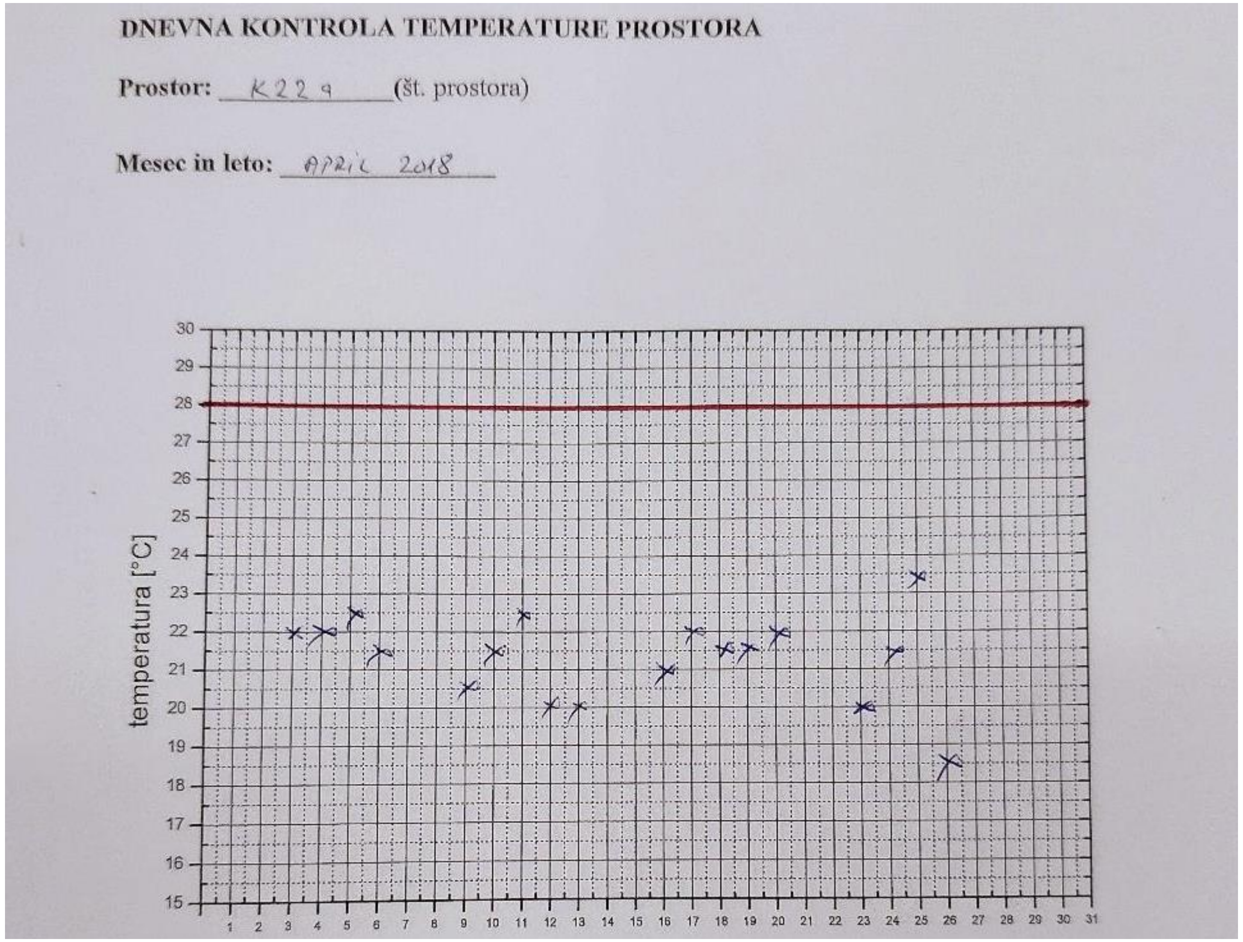
- Experimental data
- QA/QC charts
- Producer's data (e.g. uncertainty of balance, pipettes, etc.)

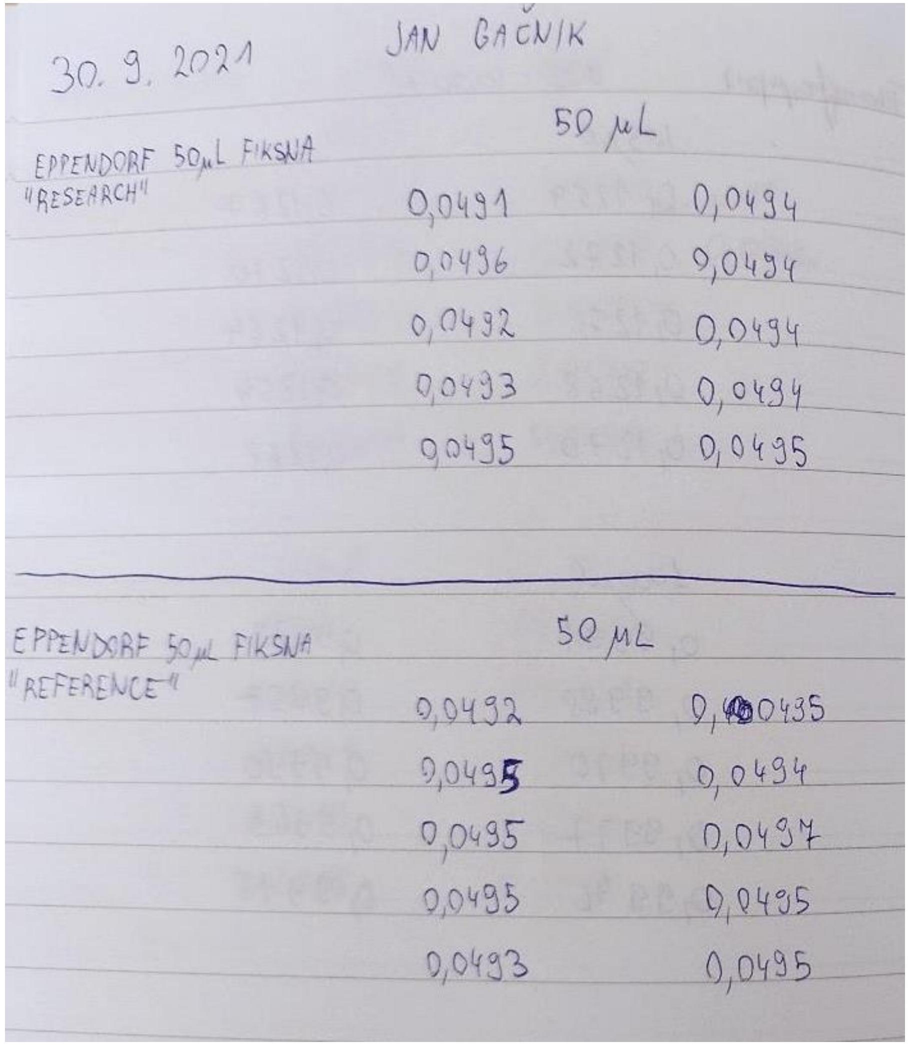
All uncertainty sources to the combined measurement uncertainty must be expressed as **standard** uncertainties.



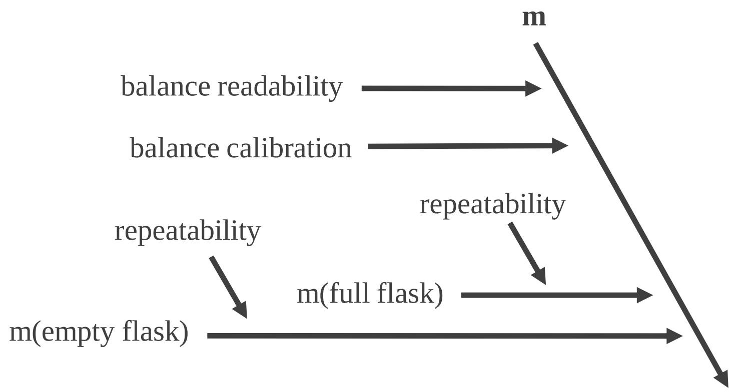
ISO-GUM approach

- Uncertainty of pipettes and volumetric flasks
- Experimental data – Log books





Uncertainty components

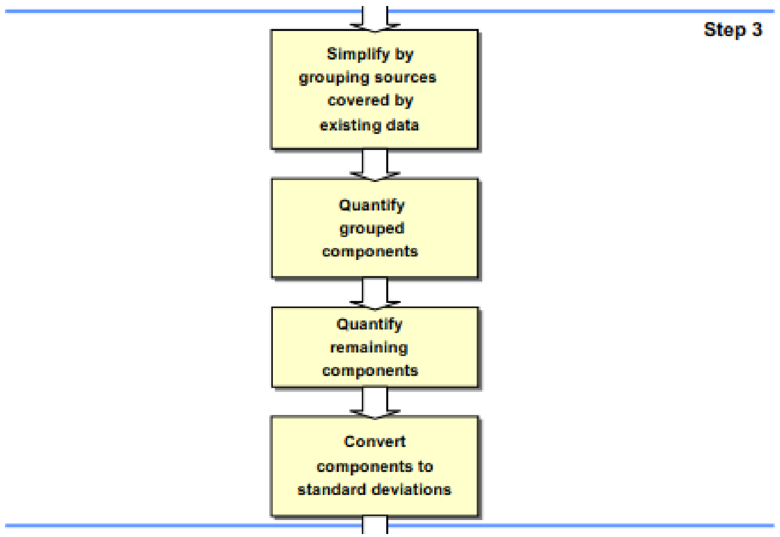


- In estimating the overall uncertainty, it may be necessary to take each source of uncertainty and treat it separately to obtain the contribution from that source

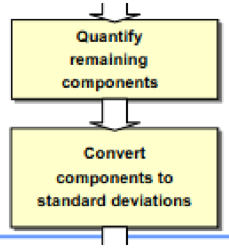
- When expressed as a standard deviation, an uncertainty component is known as a standard uncertainty

- Uncertainty is calculated separately for:

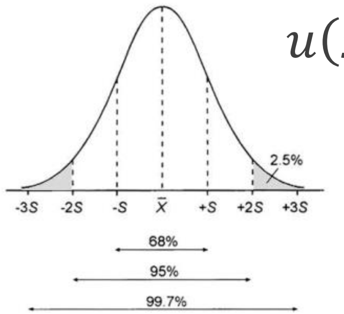
- a) Concentrations close to the limit of detection
- b) Higher concentrations



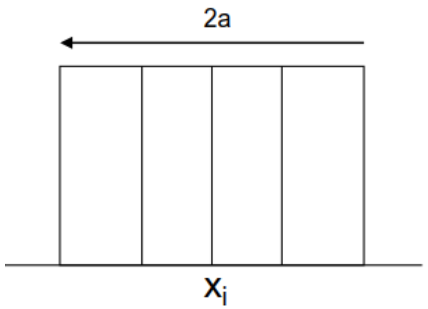
Uncertainty components



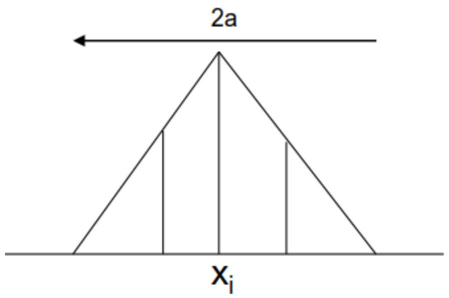
- All uncertainty contributions must be expressed as standard uncertainties, that is, as standard deviations
- Where a confidence interval is given in the form ± at p% then divide the value by the appropriate percentage point of the normal distribution to calculate the standard deviation
- If limits of ±a are given without a confidence level and there is reason to expect that extreme values are likely, it is normally appropriate to assume a rectangular distribution
- If limits of ±a are given without a confidence level, but there is reason to expect that extreme values are unlikely, it is normally appropriate to assume a triangular distribution



$$u(x_i) = \frac{S}{k}$$



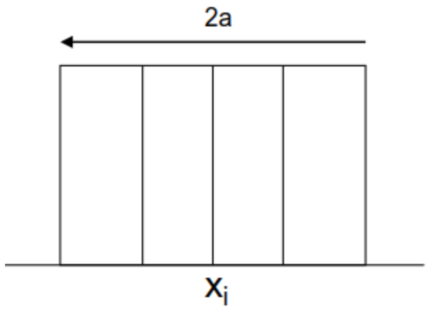
$$u(x_i) = \frac{a}{\sqrt{3}}$$



$$u(x_i) = \frac{a}{\sqrt{6}}$$

Uncertainty components

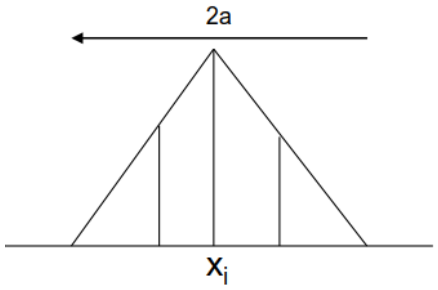
- Common for Type B



- Rectangular distribution
- e.g. scale of the instrument, balance

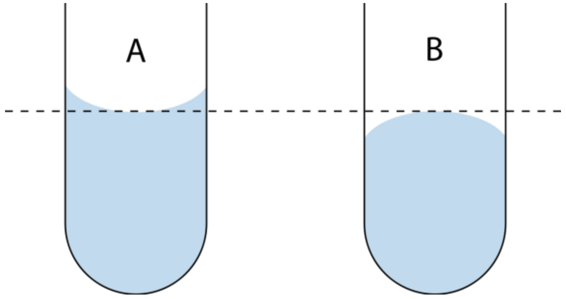
$$u(m, read) = \frac{a}{\sqrt{3}} = \frac{?}{\sqrt{3}}$$

10.955 – 10.964 g



- Triangular distribution
- e.g. pipettes, volumetric flasks

$$u(V, cal) = \frac{a}{\sqrt{6}} = \frac{?}{\sqrt{6}}$$



ISO-GUM approach

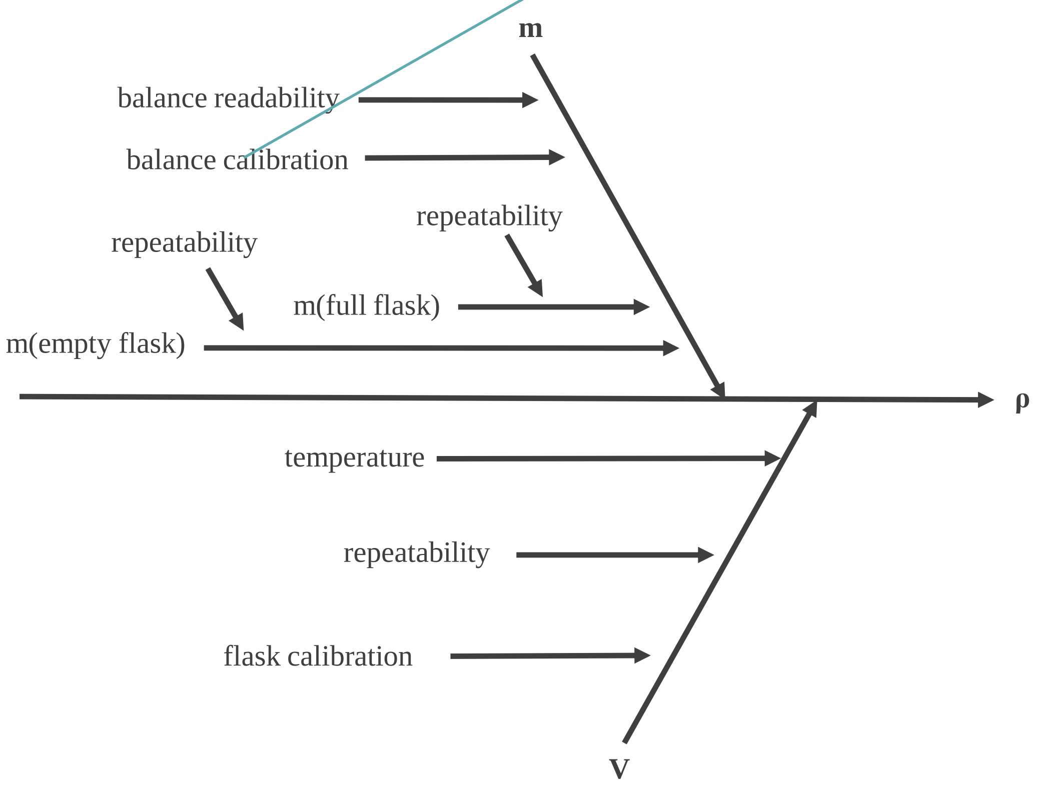
- Uncertainty of pipettes and volumetric flasks

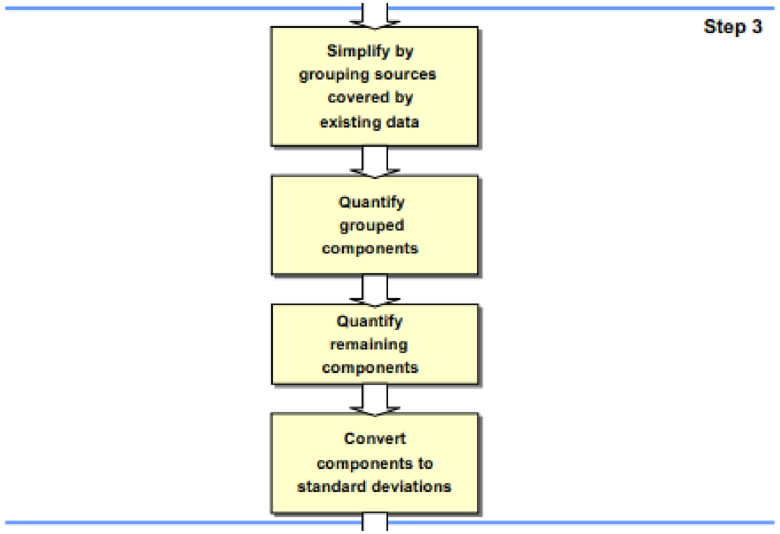
uncertainty due to repeatability				uncertainty due to temperature			
V				V (mL)	±ΔT (°C)	u	u(r)
m (g)	Average	u	u(r)	500.00	4	0.2425	0.0485%
498.2							
501.5							
501.1				u_{temp}	$u_{temp} = \frac{V \cdot \gamma \cdot \Delta t}{\sqrt{3}}$		
503.3							
502.2	501.1	1.5166	0.3026%				
499.9							
501.0				Flask calibration			
500.3				V (mL)		u	u(r)
502.4				500	0.25	0.102	0.0354%

	γ / $°C^{-1}$
H_2O	$2.1 \cdot 10^{-4}$
EtOH	$1.4 \cdot 10^{-3}$

ISO-GUM approach – Step 3: Quantify Uncertainty Components

Manufacturer certificate





Repeatability: experimental data
Standard deviation

5.47
5.66
4.97
5.34
5.08
5.13
5.37
5.40
4.96

ISO-GUM approach

- Reproducibility (intermediate precision)
- Grouped samples in the similar concentration range

$$u(rep) = \frac{standard\ deviation}{\sqrt{n}} = 0.059$$

n – number of parallel measurements, not samples

$$\rho = \frac{m}{V} * F_{rep}$$

Sample	R1	R2	mean	R1-R2	(R1-R2)/mean
Sample1	105.61	107.88	106.75	-2.27	-0.02
Sample2	109.60	110.23	109.91	-0.62	-0.01
Sample3	83.25	81.94	82.59	1.31	0.02
Sample4	90.24	82.17	86.21	8.07	0.09
Sample5	97.02	90.04	93.53	6.98	0.07
Sample6	131.30	128.91	130.10	2.38	0.02
Sample7	132.16	133.03	132.60	-0.86	-0.01
Sample8	90.24	82.17	86.21	8.07	0.09
Sample9	73.01	77.93	75.47	-4.92	-0.07
Sample10	111.02	110.91	110.96	0.11	0.00
Sample11	134.65	124.81	129.73	9.84	0.08
Sample12	69.37	68.32	68.84	1.06	0.02
Sample13	80.95	69.40	75.17	11.56	0.15
Sample14	144.67	168.93	156.80	-24.26	-0.15
Sample15	219.43	184.29	201.86	35.13	0.17

- See: Eurachem, example A4

ISO-GUM approach – Step 4: Calculate Combined Uncertainty

- The standard uncertainty of y, where y is the estimate of the measurand Y and thus the result of the measurement, is obtained by appropriately combining the standard uncertainties of the input estimates $x_1, x_2, \ldots, x_N$. This combined standard uncertainty of the estimate y is denoted by $u_c(y)$.

- $u_c(y) = \sqrt{\sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 * u^2(x_i)}$ or $u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 * u^2(x_i)$

- Each $u(x_i)$ is a standard uncertainty evaluated as Type A or Type B uncertainty

- The partial derivatives $\partial f/\partial x_i$ are equal to $\partial f/\partial X_i$ evaluated at $X_i = x_i$
- These derivatives, called sensitivity coefficients, describe how the output estimate y varies with changes in the values of the input estimates $x_1, x_2, \ldots, x_N$

Combined standard uncertainty - example

- Density = *f* (mass, volume)
- $y = \frac{x_1}{x_2}$ $\rho = \frac{m}{V}$
- $u_c^2\,(\rho) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 * u^2(x_i) = \left(\frac{\partial \rho}{\partial m}\right)^2 * u^2(m) + \left(\frac{\partial \rho}{\partial V}\right)^2 * u^2(V)$
- Calculating all partial derivations for more complex model equations – time consuming
- Math shortcuts

Combined standard uncertainty - example

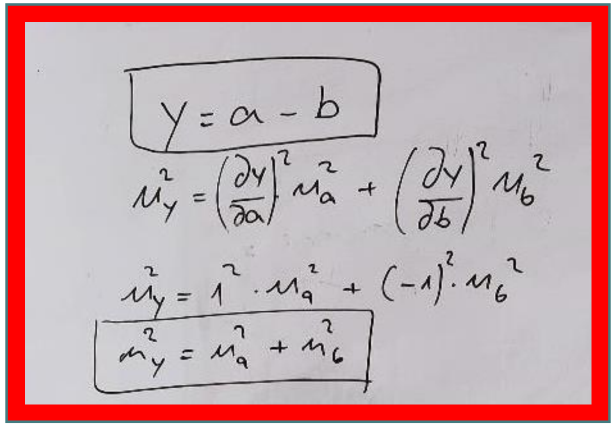
- $u_c^2\,(\rho) = \left(\frac{\partial\rho}{\partial m}\right)^2 * u^2(m) + \left(\frac{\partial\rho}{\partial V}\right)^2 * u^2(V)$
- $\frac{\partial\rho}{\partial m} = \frac{1}{V} \qquad \frac{\partial\rho}{\partial V} = \frac{-m}{V^2}$
- $u_c^2\,(\rho) = \left(\frac{1}{V}\right)^2 * u^2(m) + \left(\frac{-m}{V^2}\right)^2 * u^2(V) \qquad \Big| : \rho^2$
- $\frac{u_c^2\,(\rho)}{\rho^2} = \frac{1}{V^2\rho^2} * u^2(m) + \frac{+m^2}{V^4\rho^2} * u^2(V)$
- $\frac{u_c^2\,(\rho)}{\rho^2} = \frac{1}{V^2 * \frac{m^2}{V^2}} * u^2(m) + \frac{m^2}{V^4 * \frac{m^2}{V^2}} * u^2(V)$
- $\frac{u_c^2\,(\rho)}{\rho^2} = \frac{u^2(m)}{m^2} + \frac{u^2(V)}{V^2}$
- $\frac{u_c\,(\rho)}{\rho} = \sqrt{\frac{u^2(m)}{m^2} + \frac{u^2(V)}{V^2}}$
- $u_{c,r}^2(\rho) = u_r^2(m) + u_r^2(V)$ where $u_r^2(x_i) = \frac{u^2(x_i)}{x_i^2}$

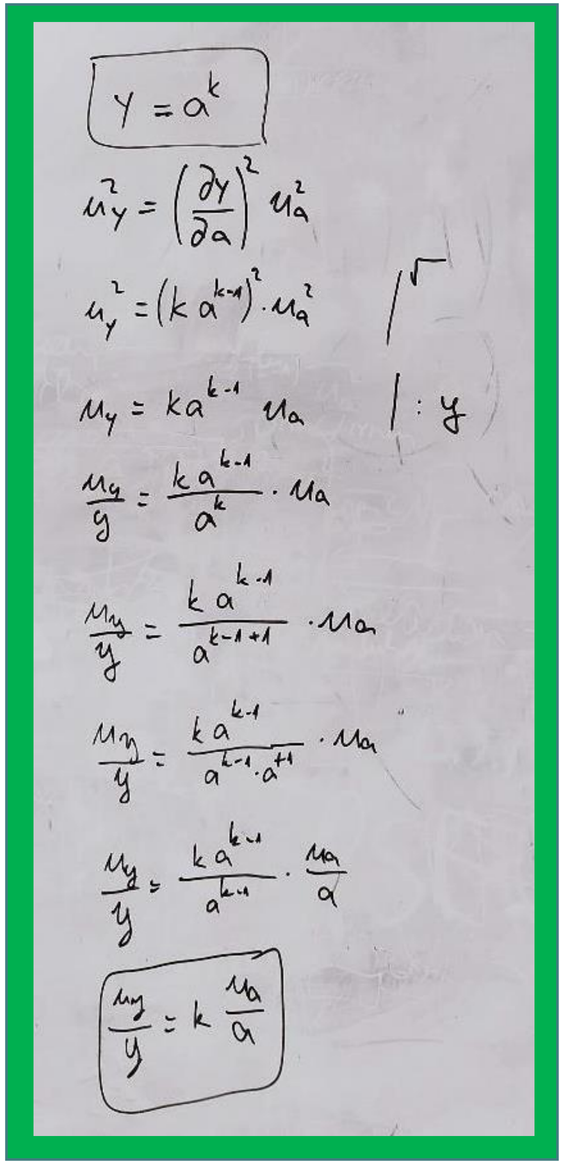
Valid for multiplication and division operation
e.g.
ρ = m/V

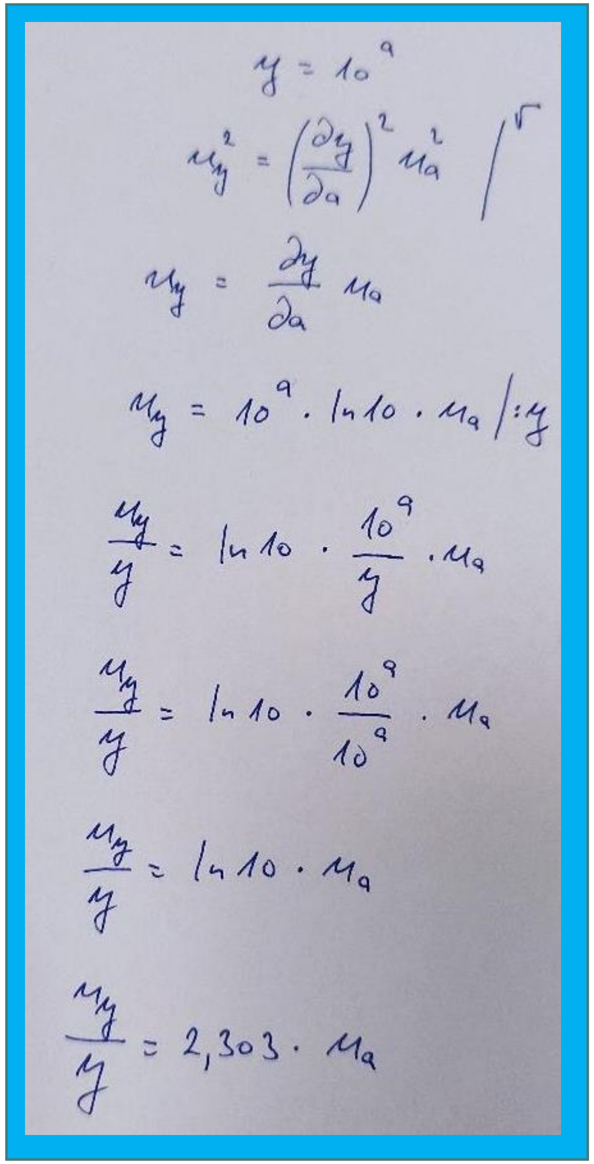
Uncertainty propagation in arithmetic calculations

Type of calculation	Model example for y = f (a,b,c)	Uncertainty of y
Addition or subtraction	$y = a + b - c$	$u_y = \sqrt{u_a^2 + u_b^2 + u_c^2}$
Multiplication or division	$y = a * {}^{b}/_{c}$	$\frac{u_y}{y} = \sqrt{\left(\frac{u_a}{a}\right)^2 + \left(\frac{u_b}{b}\right)^2 + \left(\frac{u_c}{c}\right)^2}$
Exponentiation	$y = a^k$	$\frac{u_y}{y} = \mathrm{k} * \frac{u_a}{a}$
Logarithm	$y = log_{10}a$	$u_y = 0.434 * \frac{u_a}{a}$
Anti-logarithm	$y = 10^a$	$\frac{u_y}{y} = 2.303 * u_a$

Uncertainty propagation in arithmetic calculations







Model example for y = f (a,b,c)	Uncertainty of y
$y = a + b - c$	$u_y = \sqrt{u_a^2 + u_b^2 + u_c^2}$
$y = a * {}^{b}/_{c}$	$\frac{u_y}{y} = \sqrt{\left(\frac{u_a}{a}\right)^2 + \left(\frac{u_b}{b}\right)^2 + \left(\frac{u_c}{c}\right)^2}$
$y = a^k$	$\frac{u_y}{y} = \mathrm{k} * \frac{u_a}{a}$
$y = log_{10} a$	$u_y = 0.434 * \frac{u_a}{a}$
$y = 10^a$	$\frac{u_y}{y} = 2.303 * u_a$

Uncertainty propagation in arithmetic calculations

$$y = \frac{a-b}{c}$$

Model example for y = f (a,b,c)	Uncertainty of y
$y = a + b - c$	$u_y = \sqrt{u_a^2 + u_b^2 + u_c^2}$
$y = a * {}^{b}/_{c}$	$\frac{u_y}{y} = \sqrt{\left(\frac{u_a}{a}\right)^2 + \left(\frac{u_b}{b}\right)^2 + \left(\frac{u_c}{c}\right)^2}$

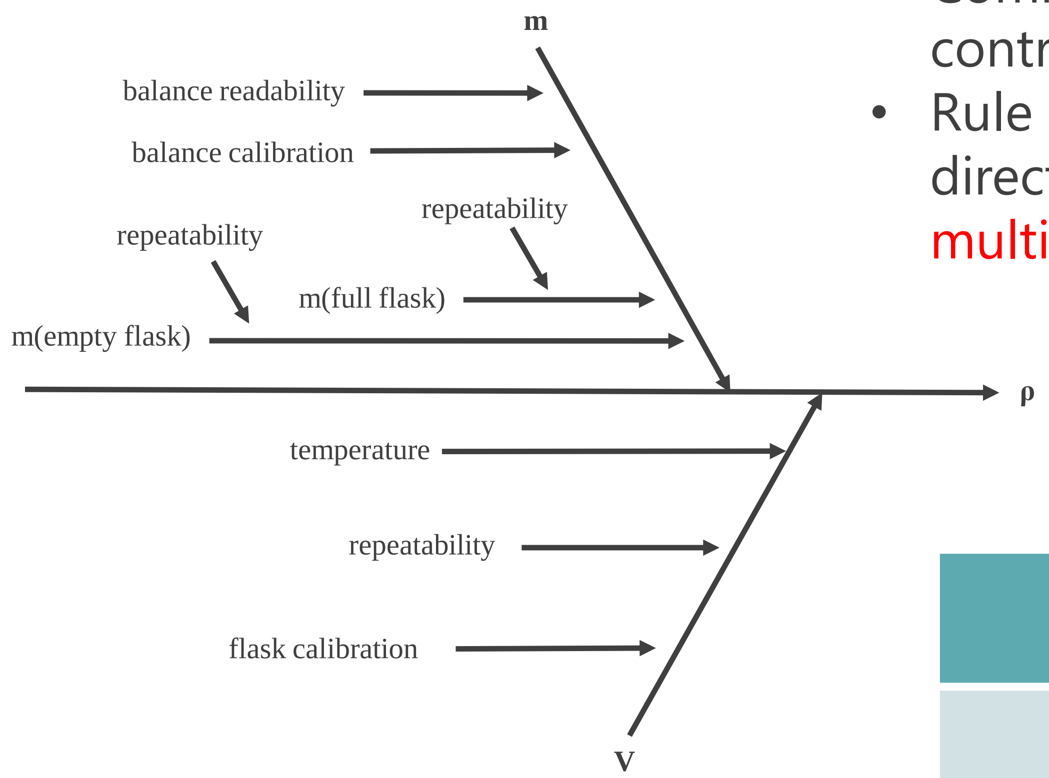
$$u_{ab} = \sqrt{u_a^2 + u_b^2}$$

$$u_{r,ab} = \frac{u_{ab}}{a-b} \qquad u_{r,c} = \frac{u_c}{c}$$

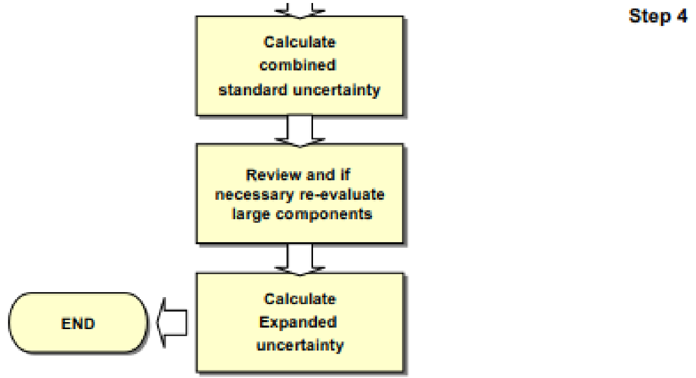
$$u_{r,y} = \sqrt{u_{r,ab}^2 + u_{r,c}^2}$$

	y	a-b	a	b	c
Value	**1**	25	65	40	25
u	**0.5**	=sqrt(6^2+8^2)= 10	6	8	7.5
$u_r = \frac{u}{value}$	=sqrt(0.4^2+0.3^2) = 0.5	0.4	0.09	0.2	0.3

ISO-GUM approach



- Combine (pool) all uncertainty contributions
- Rule of thumb: for sources not directly in the model, assume multiplication



Model example for y = f (a,b,c)	Uncertainty of y
$y = a + b - c$	$u_y = \sqrt{u_a^2 + u_b^2 + u_c^2}$
$y = a * {}^{b}/_{c}$	$\frac{u_y}{y} = \sqrt{\left(\frac{u_a}{a}\right)^2 + \left(\frac{u_b}{b}\right)^2 + \left(\frac{u_c}{c}\right)^2}$

ISO-GUM approach

- Pooling uncertainties for Volume

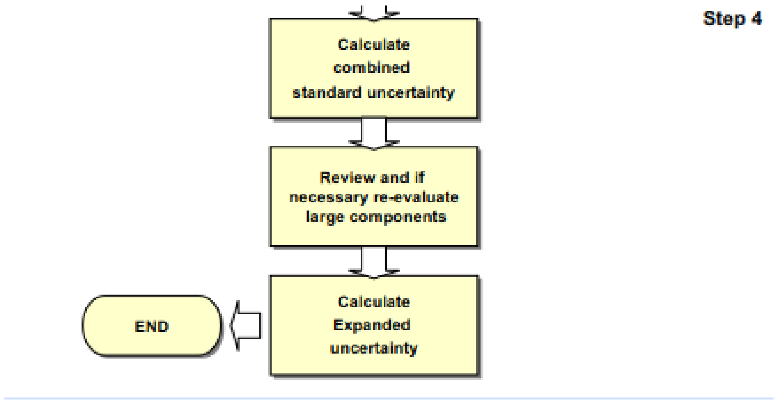
<table>
<tr><td colspan="4">uncertainty due to repeatability</td><td colspan="4">uncertainty due to temperature</td></tr>
<tr><td colspan="4">V</td><td>V (mL)</td><td>±ΔT (°C)</td><td>u</td><td>u(r)</td></tr>
<tr><td>m (g)</td><td>Average</td><td>u</td><td>u(r)</td><td>500.00</td><td>4</td><td>0.2425</td><td>0.0485%</td></tr>
<tr><td>498.2</td><td rowspan="9">501.1</td><td rowspan="9">1.5166</td><td rowspan="9">0.3026%</td><td colspan="4" rowspan="6"></td></tr>
<tr><td>501.5</td></tr>
<tr><td>501.1</td></tr>
<tr><td>503.3</td></tr>
<tr><td>502.2</td></tr>
<tr><td>499.9</td></tr>
<tr><td>501.0</td><td colspan="4">Flask calibration</td></tr>
<tr><td>500.3</td><td>V (mL)</td><td></td><td>u</td><td>u(r)</td></tr>
<tr><td>502.4</td><td>500</td><td>0.25</td><td>0.102</td><td>0.0354%</td></tr>
</table>

$$\frac{u_V}{V} = \sqrt{{u_{r,repeat}}^2 + {u_{r,T}}^2 + {u_{r,cal}}^2}$$

ISO-GUM approach – Step 4: Calculate Combined Uncertainty

- Uncertainty contributions must be expressed as standard uncertainties
- Relative combined standard uncertainty, $u_{r,c}$
- $u_c(y) = \sqrt{\sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 * u^2(x_i)}$

$$u_{r,\rho} = \frac{u_\rho}{\rho} = \sqrt{\left(\frac{u_m}{m}\right)^2 + \left(\frac{u_V}{V}\right)^2 + {u_{rep}}^2}$$



ISO-GUM approach – Step 5: Expression of result

- Result: Average ± expanded uncertainty (k = 2)

$$\bar{x} \pm U\ (k = 2)$$

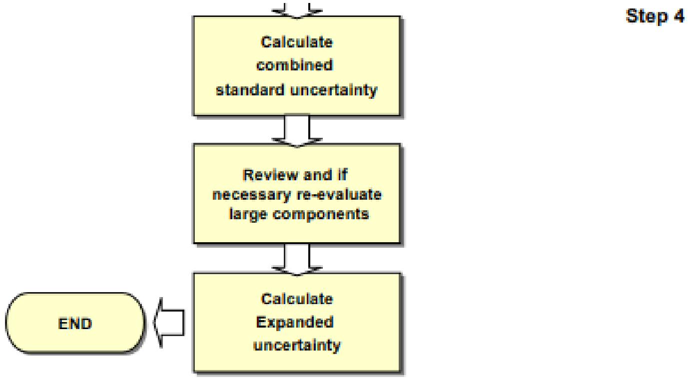
k – coverage factor

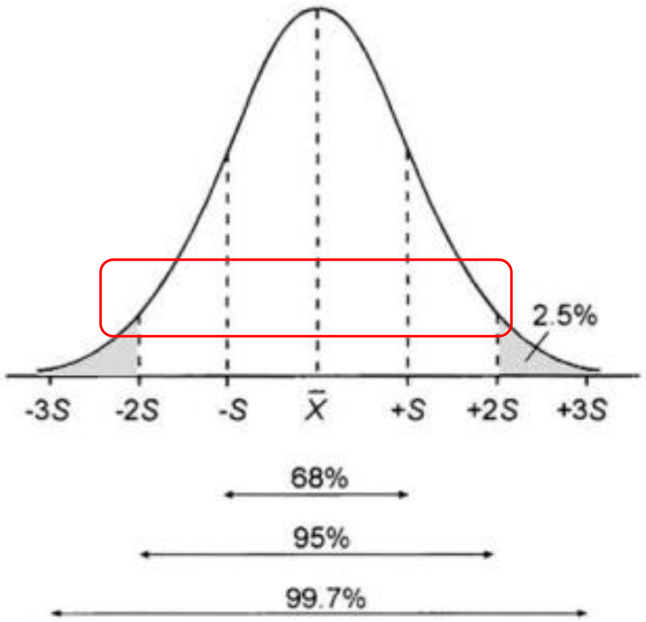
The choice of the factor k is based on the level of confidence desired. For an approximate level of confidence of 95%, k is 2.

$$U = k * u_c$$
$$U_r = k * u_{r,c}$$

ρ = 1.05 ± 0.07 g cm^{-3} (k = 2)

Takes into an account („covers the surface") 95% of probability that the result will be in the specified range.





ISO-GUM approach – Step 6: Determining contributions (index) to combined uncertainty

- How much each uncertainty source contribute to expanded combined standard uncertainty

$$contribution\ index = \frac{u_r^2(x_i)}{\sum_i u_r^2(x_i)} * 100\%$$

parameter	Index (%)
Mass	30
Volume	30
Reproducibility	40

- (Eurachem)

3.4 Practical Example 1

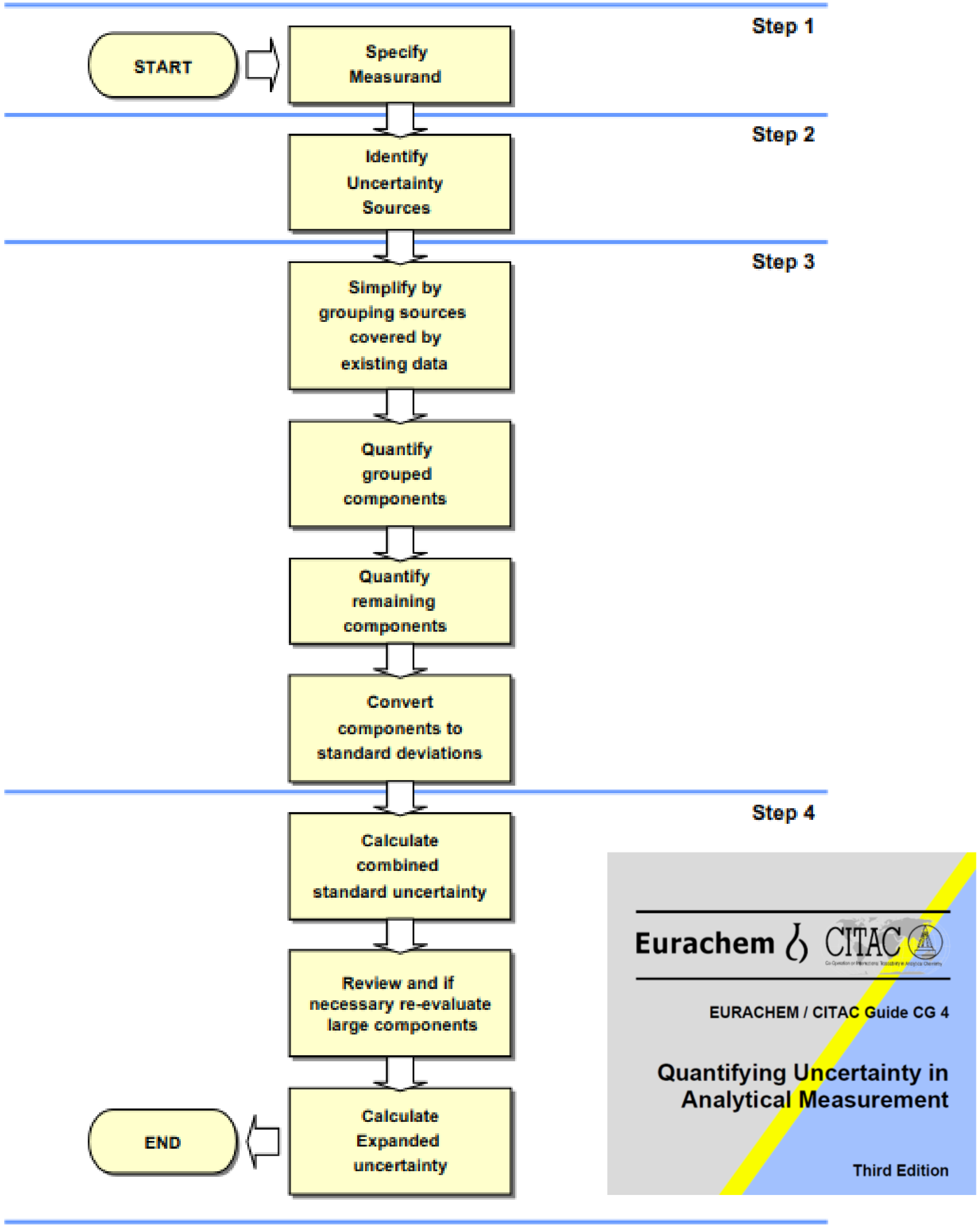
This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement no. 860497.

4 Practical Example 1

ISO-GUM approach

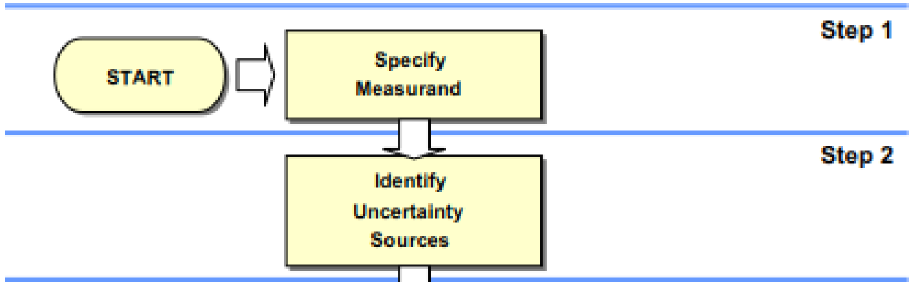
- Step 1: Specify Measurand
- Step 2: Identify Uncertainty Sources
- Step 3: Quantify Uncertainty Components
- Step 4: Calculate Combined Uncertainty

- Practical Example 1: Determination of MeHg concentration in seawater by hydride generation



ISO-GUM approach – Step 1: Specify Measurand

- The objective of a **measurement** is to determine the value of the **measurand** that is, the value of the **particular quantity** to be measured. A measurement therefore begins with an appropriate specification of the measurand, the **method of measurement**, and the **measurement procedure** (BIPM, 2008).



- Example 1:
- Analyte: methylmercury (MeHg)
- Measurand: the concentration of methylmercury in seawater
- Particular quantity: MeHg concentration in seawater in pmol/L
- Method of measurement: Cold vapor atomic fluorescence spectrometry
- Measurement procedure: SOP for the determination of MeHg concentration in seawater by hydride generation

SOP

Sampling

↓

Preservation of sample (with HCl)

↓

Derivatization with $NaBH_4$ (Quantitative recoveries)

↓

Preconcentration on GC column immersed in $N_2(l)$

↓

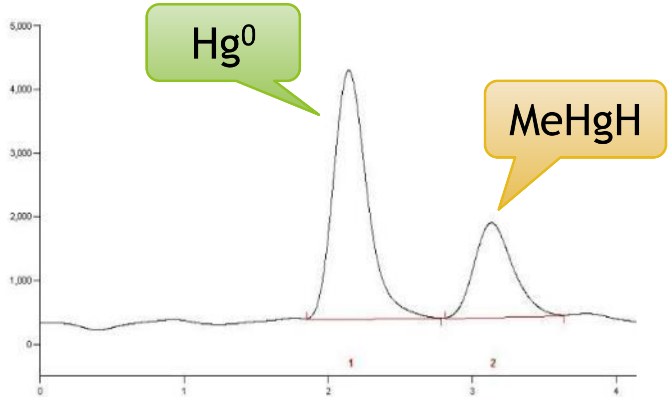
Separation of Hg species on GC column

↓

Pyrolysis

↓

Detection (CVAFS)



- Quantitative expression (**model equation**) relating the value of the measurand to the parameters on which it depends:

$$c(MeHg) = \frac{A'(S)}{A'(Std)} * \frac{n(Std)}{V(S)} = \frac{A\,(S) - SBlk}{A\,(Std) - BBlk} * \frac{c(Std) * V(Std)}{V(S)}$$

measurand analyte

- *A′*(S) and *A′*(Std) are fluorescence signal intensities of sample and MeHg standard (corrected for corresponding blanks)
- *n*(Std) is known amount of the working MeHg standard
- *V*(S) is volume of the sample

ISO-GUM approach – Step 2: Identify Uncertainty Sources

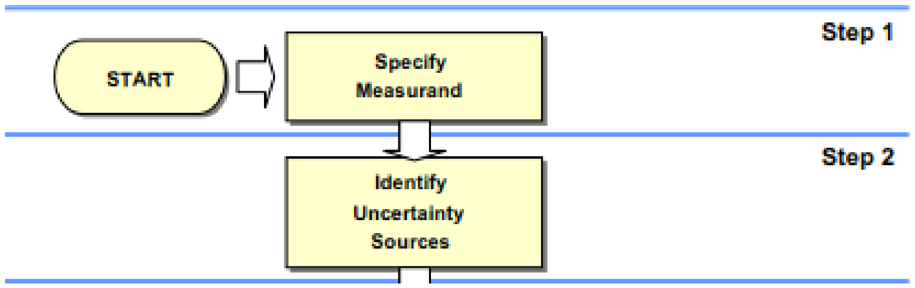
- Eurachem: „List the possible sources of uncertainty. This will include sources that contribute to the uncertainty on the parameters in the relationship specified in Step 1, but may include other sources and must include sources arising from chemical assumptions."

$$c(MeHg) = \frac{A\,(S) - SBlk}{A\,(Std) - BBlk} * \frac{c(Std) * V(Std)}{V(S)} * \frac{1}{R} * F_{rep}$$

1 by definition, but has uncertainty

≤1 by definition, but has uncertainty

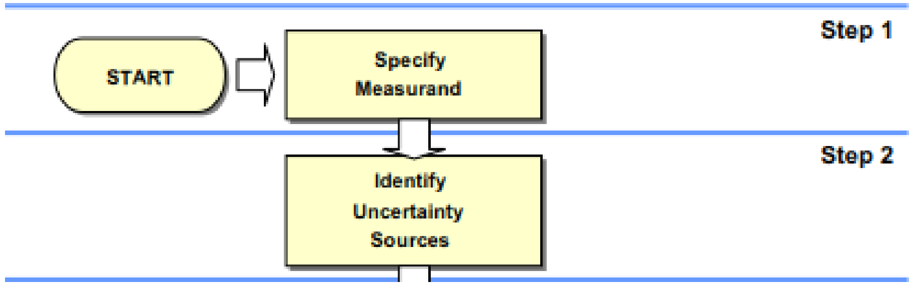
- Not all researchers include additional sources, thus artificially decreasing their uncertainy

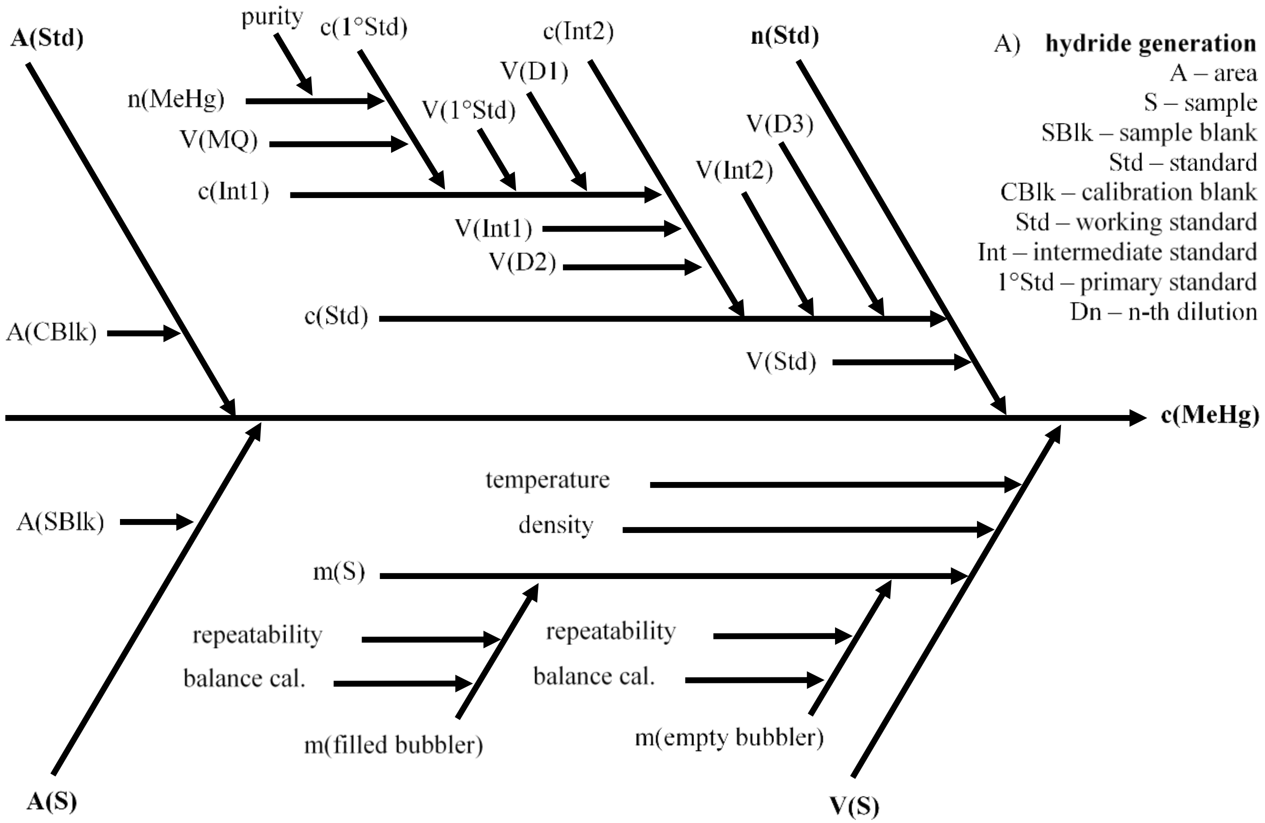


ISO-GUM approach – Step 2: Identify Uncertainty Sources

- Start with the basic expression used to calculate the measurand from intermediate values
- The cause and effect diagram – fishbone (Ishikawa) diagram

$$c(MeHg) = \frac{A'(S)}{A'(Std)} * \frac{n(Std)}{V(S)}$$

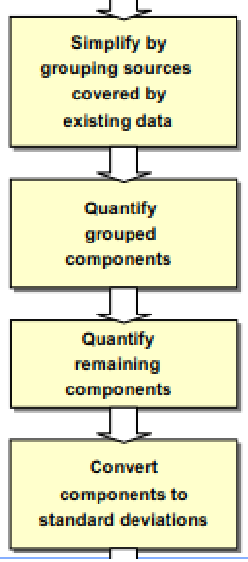




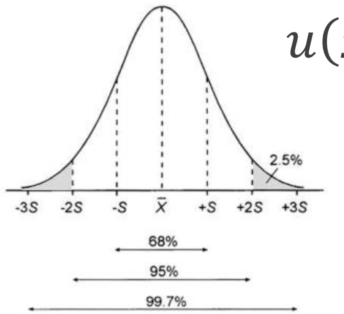
Open Excel

ISO-GUM approach – Step 3: Quantify Uncertainty Components

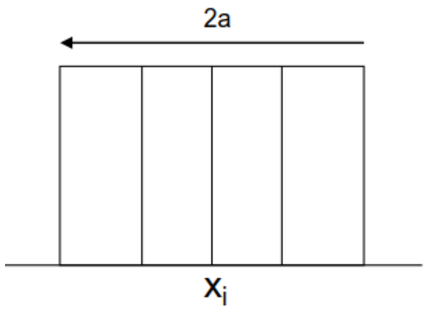
Step 3



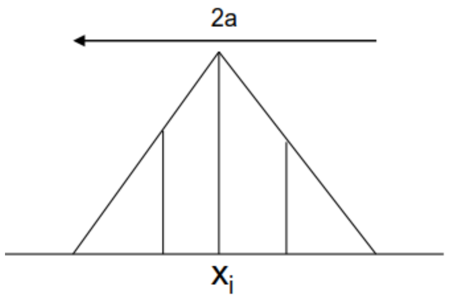
- All uncertainty contributions must be expressed as standard uncertainties, that is, as standard deviations
- Where a confidence interval is given in the form ± at p% then divide the value by the appropriate percentage point of the normal distribution to calculate the standard deviation
- If limits of ±a are given without a confidence level and there is reason to expect that extreme values are likely, it is normally appropriate to assume a rectangular distribution
- If limits of ±a are given without a confidence level, but there is reason to expect that extreme values are unlikely, it is normally appropriate to assume a triangular distribution



$$u(x_i) = \frac{S}{1.96}$$



$$u(x_i) = \frac{a}{\sqrt{3}}$$



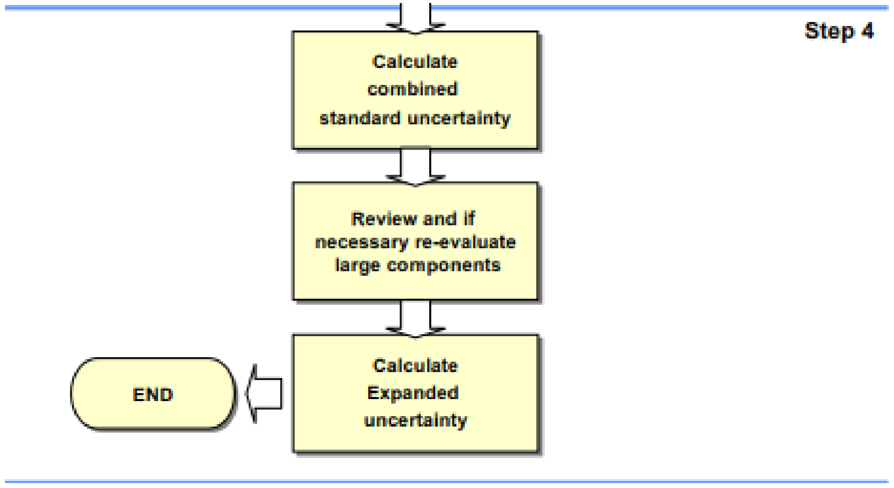
$$u(x_i) = \frac{a}{\sqrt{6}}$$

ISO-GUM approach – Step 4: Calculate Combined Uncertainty

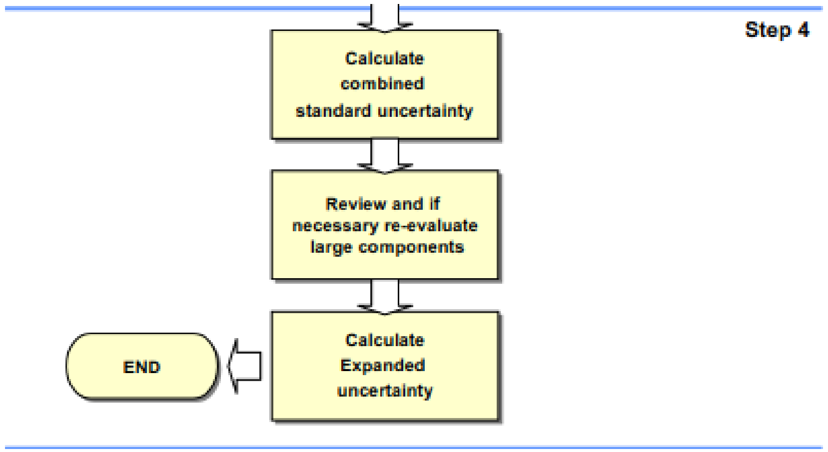
- The standard uncertainty of y:

- $u_c(y) = \sqrt{\sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 * u^2(x_i)}$ or $u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 * u^2(x_i)$

- Each $u(x_i)$ is a standard uncertainty evaluated as Type A or Type B uncertainty
- Sensitivity coefficients
- Math shortcuts



ISO-GUM approach



- Uncertainty contributions
  - Sample area repeatability
  - SBlk area repeatability
  - Correction of Sample area for its blank

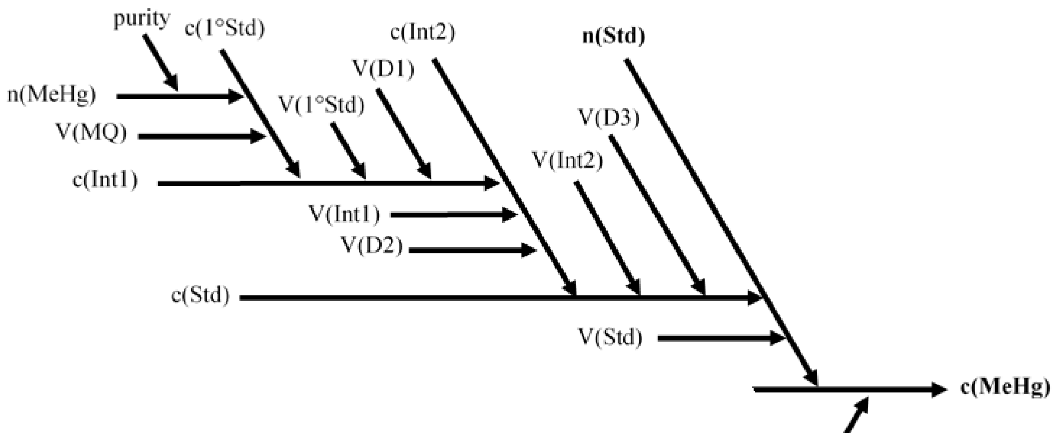
$$c(MeHg) = \frac{A\,(S) - SBlk}{A\,(Std) - BBlk} * \frac{c(Std) * V(Std)}{V(S)} * \frac{1}{R} * F_{rep}$$

- Standard deviation

Model example for y = f (a,b,c)	Uncertainty of y
$y = a + b - c$	$u_y = \sqrt{u_a^2 + u_b^2 + u_c^2}$
$y = a * {}^{b}/_{c}$	$\frac{u_y}{y} = \sqrt{\left(\frac{u_a}{a}\right)^2 + \left(\frac{u_b}{b}\right)^2 + \left(\frac{u_c}{c}\right)^2}$

ISO-GUM approach – Step 4: Calculate Combined Uncertainty

- Let's go back to our model equation and fishbone diagram



$c_1V_1 = c_2V_2$

$$n(Std) = \frac{n_0}{V_{vf0}} * \frac{V_{p1}}{V_{vf1}} * \frac{V_{p2}}{V_{vf2}} * \frac{V_{p3}}{V_{vf3}} * V_{p4}$$

Standard in mg mL^{-1}

Standard in µg mL^{-1}

Standard in ng mL^{-1}

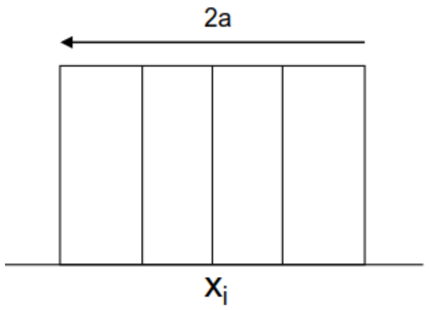
Working standard in pg mL^{-1}

p – pipette
vf – volumentric flask

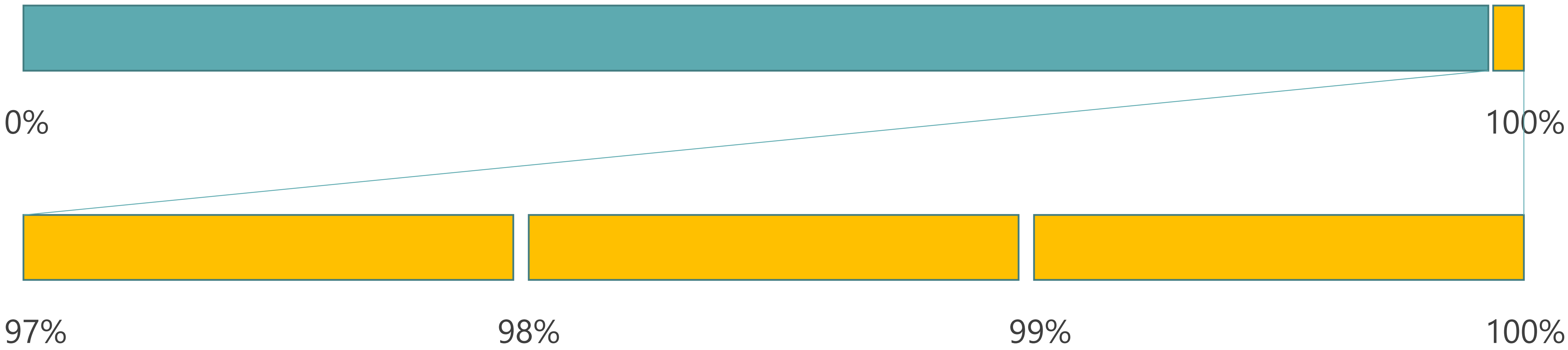
- Example: Based on fishbone diagram, n(Std) depends on primary MeHg standard (n_0, powder MeHgCl) which is dissolved and diluted three times.

ISO-GUM approach

- Uncertainty contributions
  - Purity of MeHg standard (salt)
  - Certificate: >98%



$$u(x_i) = \frac{a}{\sqrt{3}}$$



ISO-GUM approach – Step 4: Calculate Combined Uncertainty

$$n(Std) = \frac{n_0}{V_{vf0}} * \frac{V_{p1}}{V_{vf1}} * \frac{V_{p2}}{V_{vf2}} * \frac{V_{p3}}{V_{vf3}} * V_{p4}$$

Standard in mg mL^{-1}

Standard in µg mL^{-1}

Standard in ng mL^{-1}

Working standard in pg mL^{-1}

$$\frac{u[n(Std)]}{n(Std)} = \sqrt{\left[\frac{u(n_0)}{n_0}\right]^2 + \left[\frac{u(V_{vf0})}{V_{vf0}}\right]^2 + \left[\frac{u(V_{vf1})}{V_{vf1}}\right]^2 + \left[\frac{u(V_{vf2})}{V_{vf2}}\right]^2 + \left[\frac{u(V_{vf3})}{V_{vf3}}\right]^2 + \left[\frac{u(V_{p1})}{V_{p1}}\right]^2 + \left[\frac{u(V_{p2})}{V_{p2}}\right]^2 + \left[\frac{u(V_{p3})}{V_{p3}}\right]^2 + \left[\frac{u(V_{p4})}{V_{p4}}\right]^2}$$

p – pipette

vf – volumentric flask

Note: If CRM MeHg for calibration is available, the uncertainty is provided on the certificate

ISO-GUM approach – Step 4: Calculate Combined Uncertainty

Aditional uncertainty sources: MeHg spike recovery

$$u(R_m) = R_m * \sqrt{\frac{s_{n(obs)}^2}{N * n_{obs}^2} + \left(\frac{u(n_{spike})}{n_{spike}}\right)^2}$$

MeHg standard

$u(R_m)$ is standard uncertainty

R_m is the mean spike recovery

$s_{n(obs)}$ is the standard deviation of the mean observed amount of standard spike n_{obs}

N is the number of spiked samples

$u(n_{spike})$ is the uncertainty in the added amount of standard spike n_{spike}

See: Barwick, 1999 - Approaches to the evaluation of uncertainties associated with recovery

ISO-GUM approach – Step 4: Calculate Combined Uncertainty

- Reproducibility
- Grouped samples in the similar concentration range

$$u(rep) = \frac{standard\ deviation}{\sqrt{n}}$$

Sample	R1	R2	mean	R1-R2	(R1-R2)/mean
Sample1	105.61	107.88	106.75	-2.27	-0.02
Sample2	109.60	110.23	109.91	-0.62	-0.01
Sample3	83.25	81.94	82.59	1.31	0.02
Sample4	82.17	90.24	86.21	-8.07	-0.09
Sample5	90.04	97.02	93.53	-6.98	-0.07
Sample6	128.91	131.30	130.10	-2.38	-0.02
Sample7	133.03	132.16	132.60	0.86	0.01
Sample8	82.17	90.24	86.21	-8.07	-0.09
Sample9	77.93	73.01	75.47	4.92	0.07
Sample10	111.02	110.91	110.96	0.11	0.00
Sample11	134.65	124.81	129.73	9.84	0.08
Sample12	69.37	68.32	68.84	1.06	0.02
Sample13	80.95	69.40	75.17	11.56	0.15
Sample14	144.67	168.93	156.80	-24.26	-0.15
Sample15	219.43	184.29	201.86	35.13	0.17

n – number of parallel measurements, not samples

- See: Eurachem, example A4

ISO-GUM approach – Step 4: Calculate Combined Uncertainty

- Uncertainty contributions must be expressed as standard uncertainties
- Relative combined standard uncertainty, $u_{r,c}$

$$u_{r,c} = \sqrt{\sum_i \left\{\frac{\partial[MeHg]}{\partial x_i} * u_r(x_i)\right\}^2}$$

- where x_i is individual uncertainty contribution, $u_r(x_i)$ its standard uncertainty
- Simplification: For mathematical model expressed in the form of product of quotient, no need for partial derivations:

$$u_{r,c}[MeHg] = \sqrt{\begin{matrix} u_r(A'(S))^2 + u_r(V(S))^2 + u_r(A'(Std))^2 + u_r(n(Std))^2 \\ + \\ u_r(R_m)^2 + u_r(rep.(S))^2 + u_r(rep.(Std))^2 \end{matrix}}$$

ISO-GUM approach – Step 5: Expression of result

- Result: Average ± expanded uncertainty (k = 2)

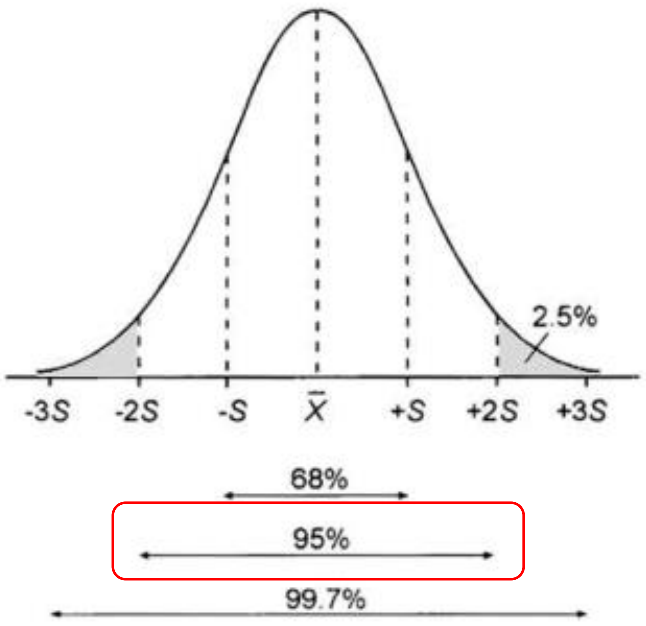
$$\bar{x} \pm U \ (k = 2)$$

k – coverage factor

The choice of the factor k is based on the level of confidence desired. For an approximate level of confidence of 95%, k is 2.

$$U = k * u_c$$
$$U_r = k * u_{r,c}$$

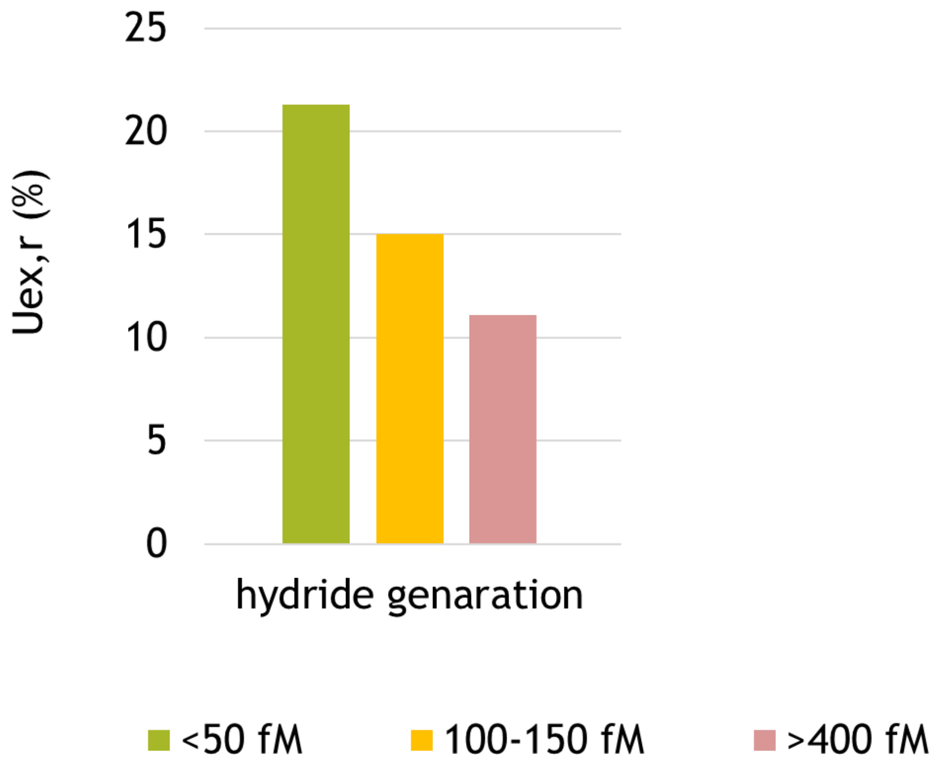
c(MeHg) = 132 ± 16.2 pg L^{-1} (k = 2)



Takes into an account („covers the surface") 95% of probability that the result will be in the specified range.

ISO-GUM approach – Step 5: Expression of result

- Expanded relative combined standard uncertainty, $U_{ex,r}$, is obtained using coverage factor 2.



$$U_{ex,r} = u_{r,c} * k$$

ISO-GUM approach – Step 6: Determining contributions (index) to combined uncertainty

- How much each uncertainty source contribute to expanded combined standard uncertainty

$$contribution\ index = \frac{u_r^2(x_i)}{\sum_i u_r^2(x_i)} * 100\%$$