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Workshop on Understanding and Evaluating Radioanalytical Measurement Uncertainty

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Measurement Uncertainty

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Workshop on
Understanding and Evaluating Radioanalytical Measurement Uncertainty

Measurement Uncertainty

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Overwiev

- Uncertainty - definition
- Uncertainty - why and when
- GUM procedure for uncertainty evaluation
- Example

Definition of uncertainty

Any measurement result is characterised by imperfections!!!

Taken from "*Guide to the Expression of Uncertainty in Measurement*" (ISO, Geneva, 1993)

"parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand" ....the uncertainty is an intrisic part of the measurement result!!!

Result = Value ± uncertainty

What is measurement uncertainty?

Is the **number** after ± in a measurement result

In the case of ^{137}Cs content in soil this is written (at a 95% confidence level) :

$^{137}Cs_{soil}$ = 100 ± 6 Bq kg^{-1}

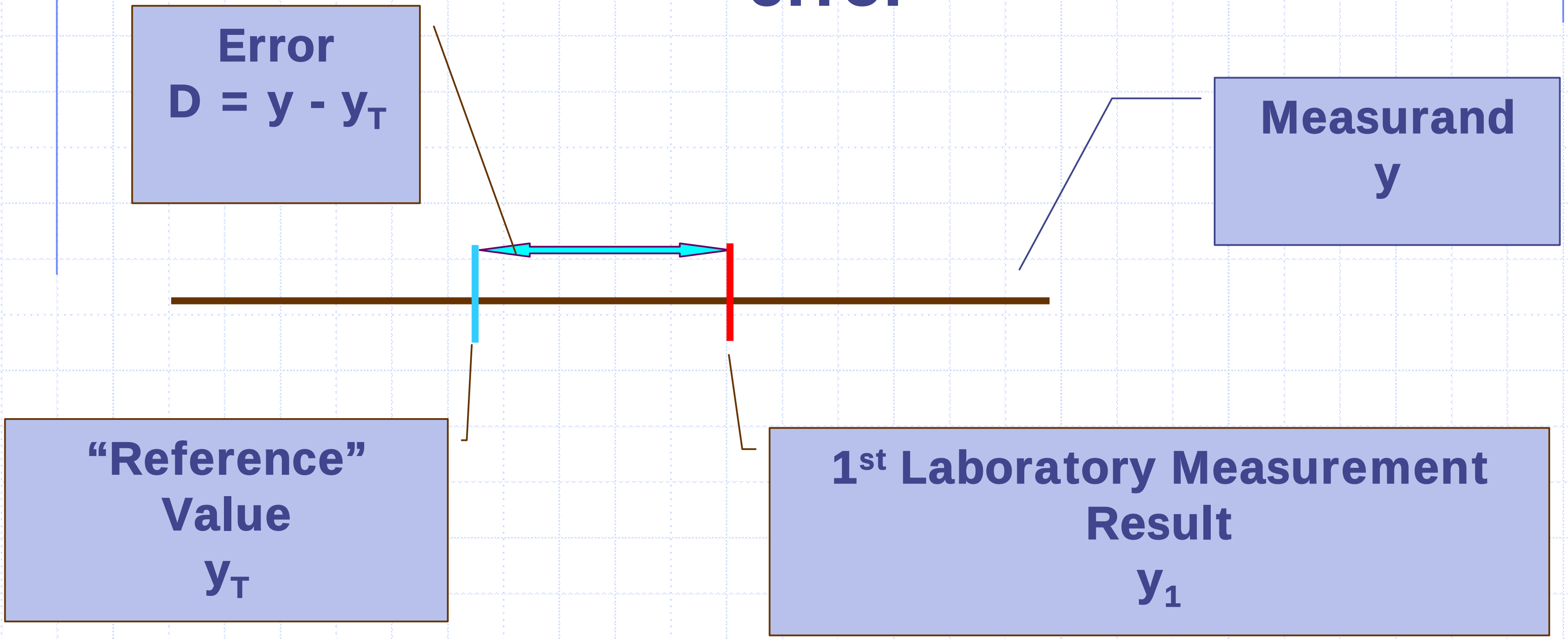
This means we are 95% sure that the content of ^{137}Cs in soil is in the range of

94 and 106 Bq kg^{-1}

(in the case of normal distribution)

What is measurement uncertainty?

All measurements are affected by a certain error



Error
$D = y - y_T$

Measurand
y

"Reference" Value
y_T

1st Laboratory Measurement Result
y_1

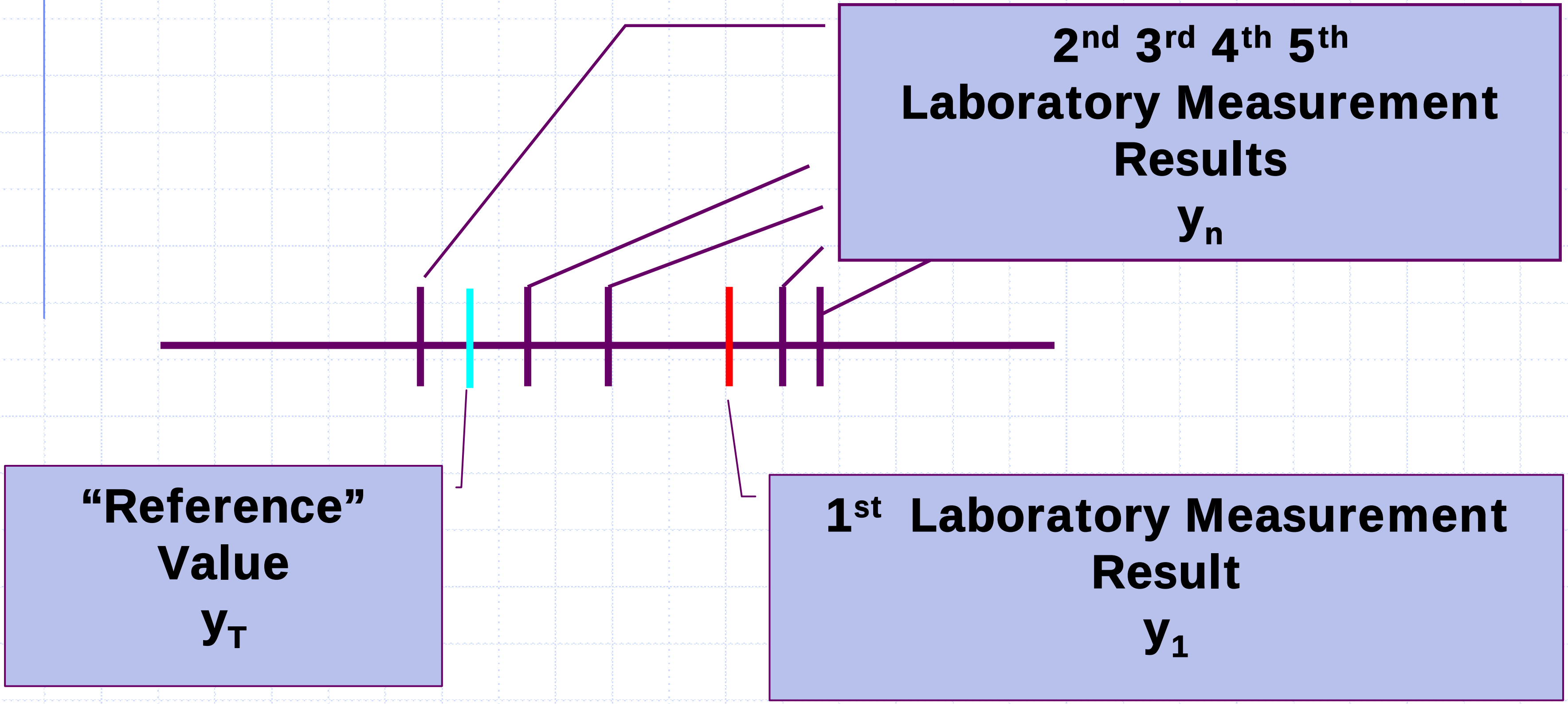
What is measurement uncertainty?

Error is the difference between the measured value and the reference (desired?) value of the object being measured

Don’t confuse the terms Error and Uncertainty

What is measurement uncertainty?

.. if we repeat the measurement 2, 3, 4, 5, times….

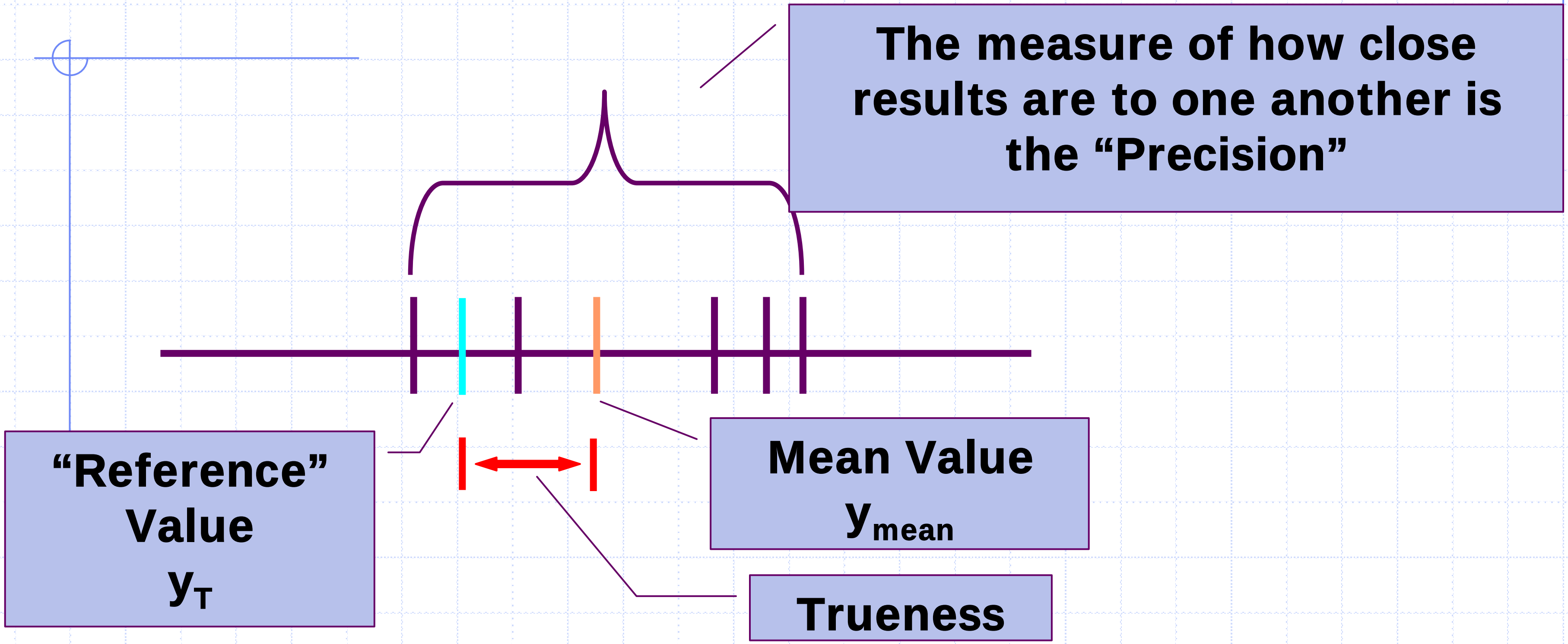


2nd 3rd 4th 5th Laboratory Measurement Results y_n

“Reference” Value y_T

1st Laboratory Measurement Result y_1

What is measurement uncertainty?



The measure of how close results are to one another is the "Precision"

"Reference" Value

y_T

Mean Value

y_{mean}

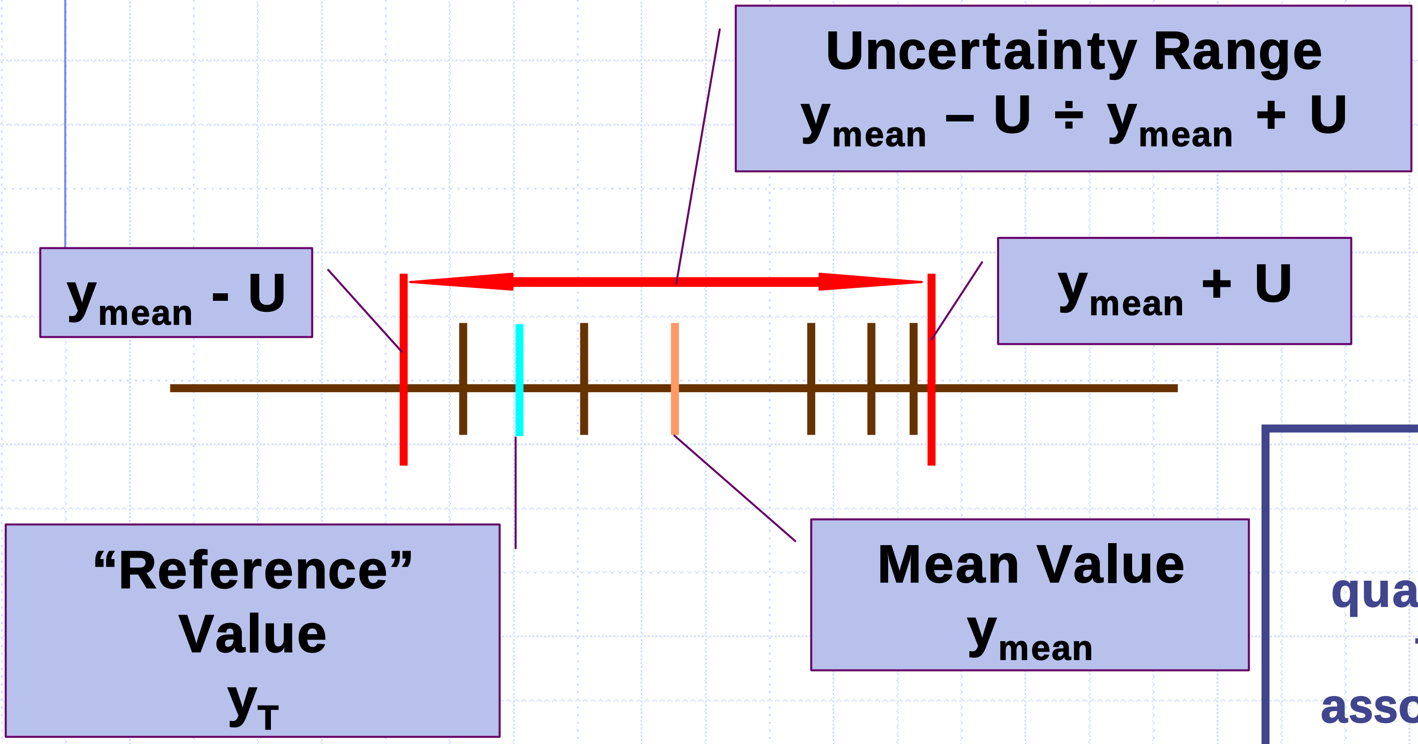
Trueness

Trueness is the closeness of
agreement between
the mean value obtained from a
large set of test results and an accepted reference value

What is measurement 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

Is a quantitative indication of the quality of the result



Uncertainty Range
$y_{mean} - U \div y_{mean} + U$

y_{mean} - U

y_{mean} + U

“Reference” Value
y_T

Mean Value
y_{mean}

It is the quantification of the doubt associated with a measurement result

It gives an answer to the question, how well does the result represent the value of the quantity being measured?

Measurement uncertainty

The uncertainty of measurement is due to:

- **<u>trueness</u>: the closeness of agreement between the average value obtained from a large series of test results and the accepted reference value**
  - **"the accepted reference value" = the true value**

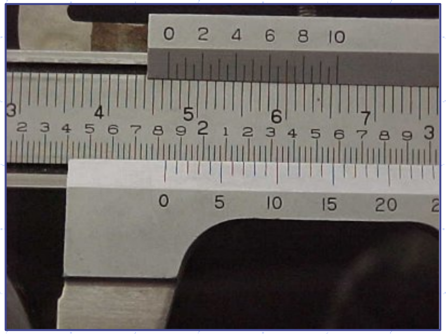
How close are the measurements to the true value?

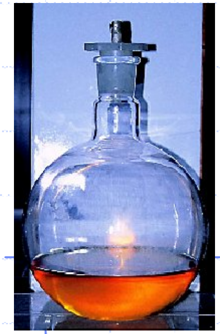
Measurement uncertainty

The uncertainty of measurement is due to:

- **precision: the closeness of agreement between independent test results obtained under stipulated conditions**
  - **repeatability: precision under similar conditions**
  - **reproducibility: precision under different conditions**

How reproducible are measurements?





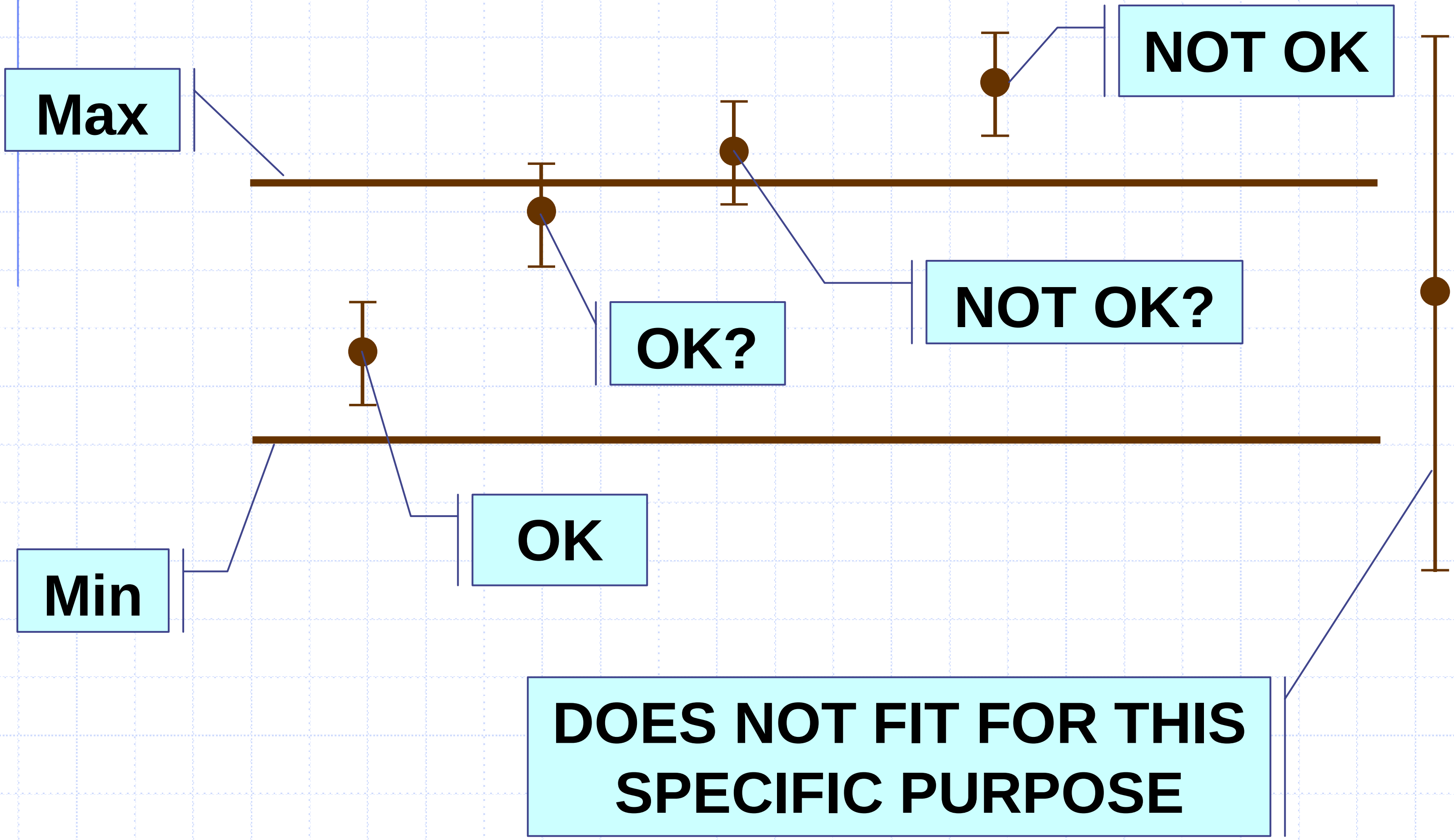
Why do we need uncertainty?

When reporting the result of a measurement it is obligatory that the quantitative indication of the uncertainty of the result be given so that those who use it can:

- demonstrate the metrological quality of the measurement
- document in transparent way the measurement procedure
- improve the knowledge about the measurement procedure
- assess the reliability and the confidence level of the result
- compare different measurement results
- understand the differences among results
- demostrate compliance with limits (legal or contractual) and the establishment of acceptance criteria

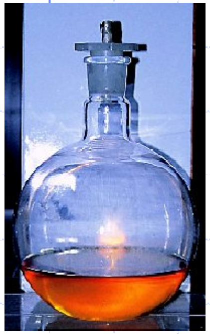
Why do we need uncertainty?

- To decide whether there is a difference between results from different laboratories, or results from the same laboratory at different occasion
- To enable a result to be interpreted with respect to a limit



When should you evaluate uncertainties of measurement results?

WHEN…



- a measurement procedure is introduced inside your laboratory
- a critical factor changes in the measurement procedure (instrument, operator, sample type…)
- during / together with procedure validation

HOW OFTEN…

- in case the laboratory needs to complain with regulation following the respective document
- in case of no guidelines available:
    - use a common sense for setting the frequency
    - monitor the data from control chart

ISO Guide GUM

- The basis of every procedure for estimating measurement uncertainty is the"Guide to the Expression of Uncertainty in Measurement" in short GUM
- The basis of any evaluation of measurement uncertainty is a statistical approach

GUM approach

Uncertainty estimation is simple in principle.

- Specify the measurand
  - Including complete equation
- Quantify significant uncertainties in all parameters
- Express as standard deviation
- Combine according to stated principles

How to apply GUM approach?

Basic Statistics:

- Probability distribution (normal, rectangular, etc.)
- Average and standard deviation of a set of data
- Law of propagation of uncertainties

(see Lecture on Basic Stastistics)

GUM approach

Specify measurand

Identify uncertainty sources

Quantify uncertainty components

Convert components to standard deviations

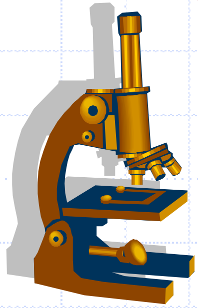
Calculate combined standard uncertainty

Review and if necessary re-evaluate large components

Calculate expanded uncertainty

Specify the measurand

1st step



In this context of uncertainty estimation, this phase requires a clear statement of what is being measured, and a quantitative expression relating the value of the measurand to the parameters on which it depends:

$$Y = f(X_1, X_2, \ldots, X_N)$$

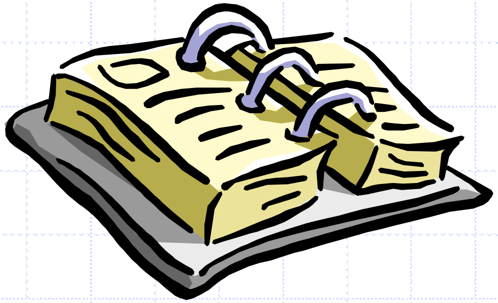
These parameters may be other measurands, quantities which are not directly measured, or constants.

NOTE:

It should be clear whether a sampling step is included within the procedure or not. If it is, estimation of uncertainties associated with the sampling procedure need to be considered

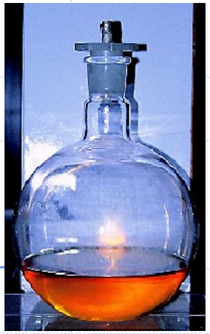
Identify uncertainty sources

2nd step



A comprehensive list of relevant sources of uncertainty should be assembled.

All the parameters which appear explicitly in the expression used to calculate the value of the measurand may have an uncertainty associated with their value and are therefore potential uncertainty sources. In addition there may be other parameters that do not appear but nevertheless affect the measurement results.

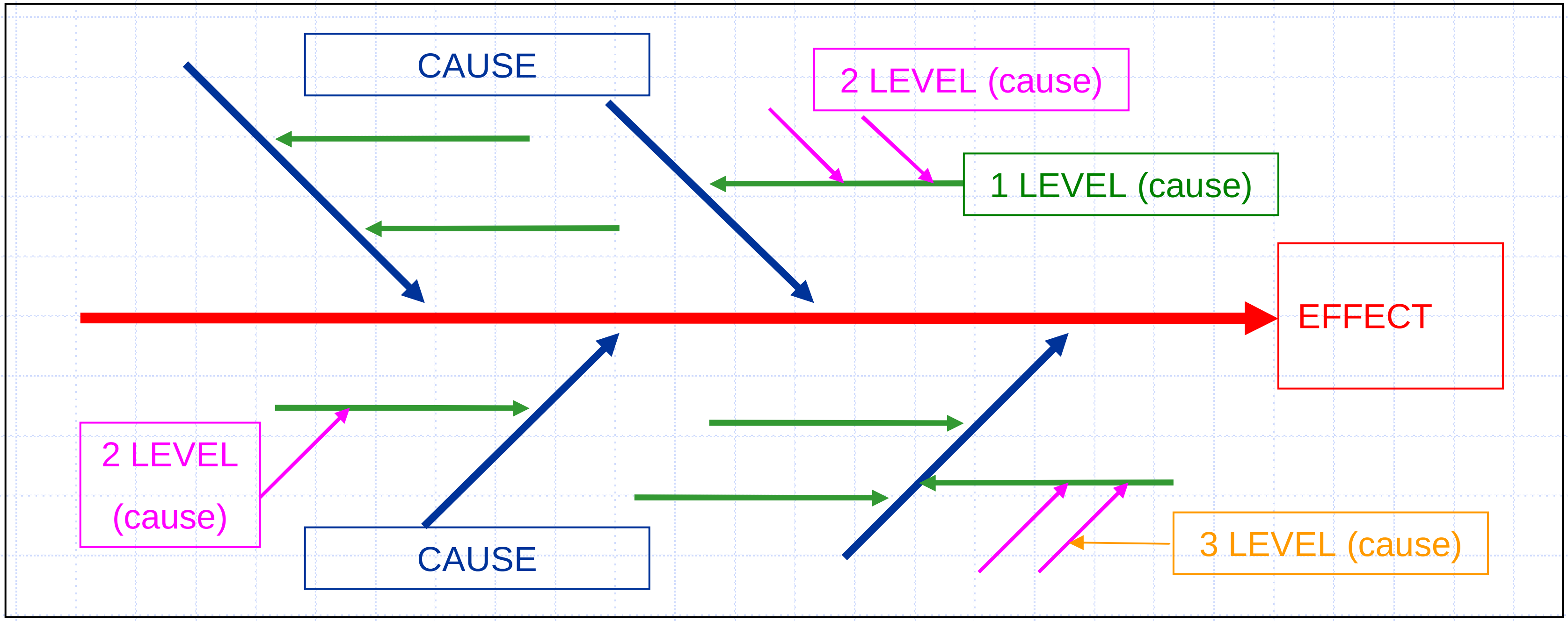


Sources of uncertainty in a measurement

- incomplete definition of the measurand
- nonrepresentative sampling – the sampled measured may not represent the defined measurand
- inadequate knowledge of the effects of environmental conditions on the measurement or imperfect measurement of environmental conditions
- personal bias in reading analogue instruments
- finite instrument resolution or discrimination threshold
- inexact values of measurement standards and reference materials
- approximations and assumptions incorporated in the measurement method and procedure
- variations in repeated observations of the measurand under apparently identical conditions

Identify uncertainty sources

The cause and effect diagram (fish-bone) is a very convenient way of listening the uncertainty sources, showing how their relate to each other and indicating their influence on the uncertainty of the result. It also helps to avoid double counting of sources.



Quantify uncertainty

3rd step

Once identified the uncertainty sources, the next step is to quantify the uncertainty arising from these sources:

- **evaluating the uncertainty arising from each individual source and converting them to standard deviation**

- **determining directly the combined contribution to the uncertainty on the result from some or all of these sources using method performance data.**

NOTE:
Not all of the components make a significant contribution to the combined uncertainty.

Convert components to standard deviations

4th step

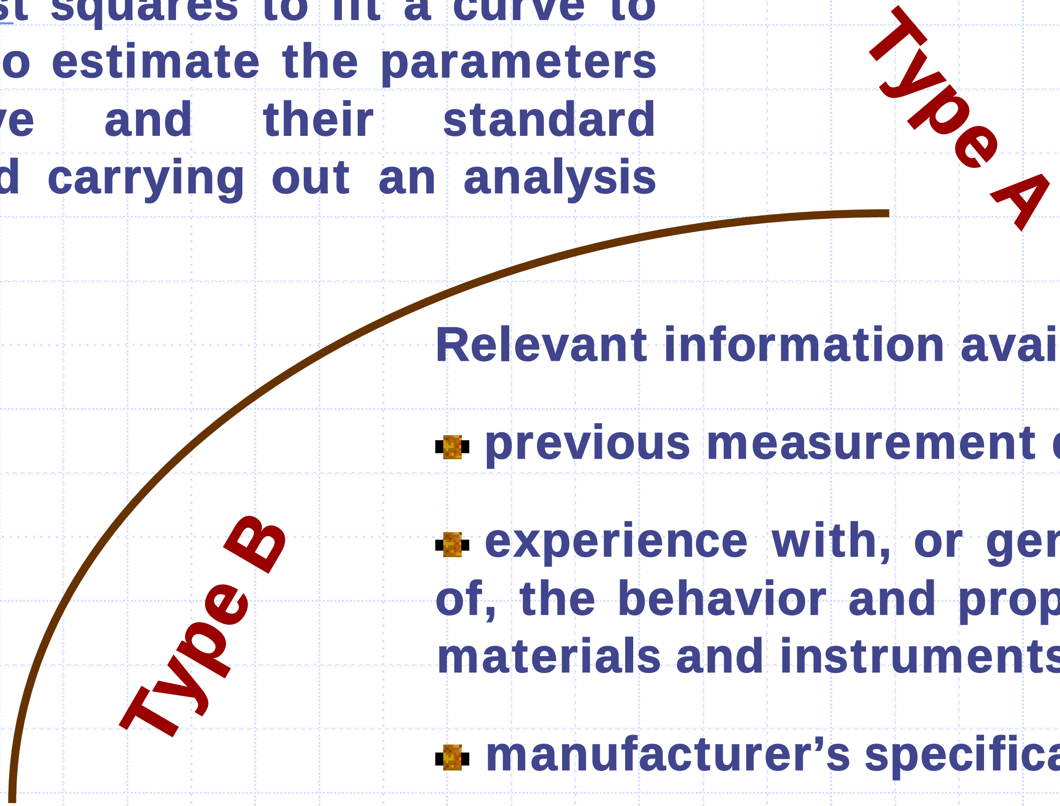
The components may be grouped into two categories according to the method used to estimate them:

A **type A** evaluation of standard uncertainty may be based on any valid statistical method for treating data.

A **type B** evaluation of standard uncertainty is usually based on scientific judgement using all of the relevant information available.

Type A and Type B

Examples are calculating the standard deviation of the mean of a series of independent observations; using the method of least squares to fit a curve to data in order to estimate the parameters of the curve and their standard deviations; and carrying out an analysis of variance



Relevant information available:

- previous measurement data
- experience with, or general knowledge of, the behavior and property of relevant materials and instruments
- manufacturer’s specifications
- data provided in calibration and other reports
- uncertainties assigned to reference data taken from handbooks

Type A

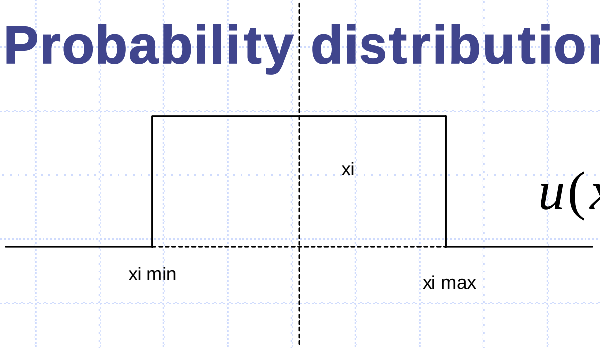
Depending on the statistical distribution of data, it is possible to estimate the corrisponding standard deviation:

	Normal	Binomial	Poisson
Standard deviation	$s_{\overline{x}} = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \overline{x})^2}{n(n-1)}}$	$s = \sqrt{np(1-p)}$	$s = \sqrt{\lambda}$

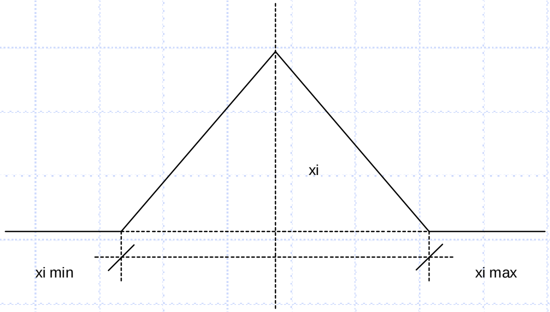
Type B

Depending on the information available, it is possible to estimate the standard uncertainty on the basis of assumed probability distributions which the input quantities approximate.

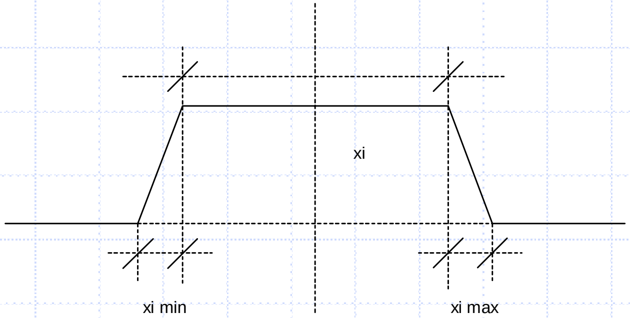
Probability distributions:



$$u(x) = \frac{x_{i\min} - x_{i\max}}{2 \cdot \sqrt{3}}$$



$$u(x) = \frac{(x_{i\min} - x_{i\max})}{2 \cdot \sqrt{6}}$$



$$\boldsymbol{u(x)} = \frac{(\boldsymbol{x}_{i\min} - \boldsymbol{x}_{i\max}) \cdot \sqrt{(1 + \beta^2)}}{2 \cdot \sqrt{6}}$$

Understanding the measurement

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

GUM § 3.4.8

Calculate the combined uncertainty

5th step

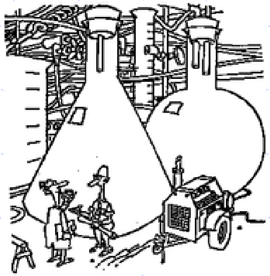
- calculate the combined standard uncertainty using the law of propagation of uncertainties (root sum of squares)
- choose the coverage factor
- calculate the expanded uncertainty multiplying the combined uncertainty by the choosen coverage factor.

Combined uncertainty

Following the law of propagation of uncertainty, the combined uncertainty can be calculated combining all the components expressed as standard deviations:

$$u_c(y) = \sqrt{\sum_{i=1}^{n}\left(\frac{\partial y}{\partial x_i}\cdot u(x_i)\right)^2 + 2\sum_{i=1}^{n-1}\sum_{j=1+1}^{n}\left(\frac{\partial y}{\partial x_i}\frac{\partial y}{\partial x_j}\cdot \mathrm{cov}(x_{ij})\right)}$$

where x_i are the input components, while cov(x_{ij}) is the covariance between x_i and x_j..



Combined uncertainty

When the input components are independent and not correlated, the covariance is zero.

The law of propagation of uncertainties can be simplyfied:

$$u_c(y) = \sqrt{\sum_{i=1}^{n} \left(\frac{dy}{dx_i} \cdot u(x_i) \right)^2}$$

Determine expanded uncertainty

The expanded uncertainty is denoted by U:

$$U(y) = k \cdot u_c(y)$$

The expanded uncertainty is required to provide an interval which may be expected to encompass a large fraction of the distribution of values which could reasonably be attributed to the measurand.

Choosing a coverage factor:

- **the level of confidence required**
- **any knowledge of the underlying distributions**
- **any knowledge of the number of values used to estimate random effects**

In general, k is in the range 2 to 3

Reporting uncertainty

A complete report of a measurement should include:

- a description of the methods used to calculate the measuremet result and its uncertainty from the experimental observations and input data
- a list of all components of uncertainty with full documentation on how each was evaluated

The result of a measurement is expressed as:

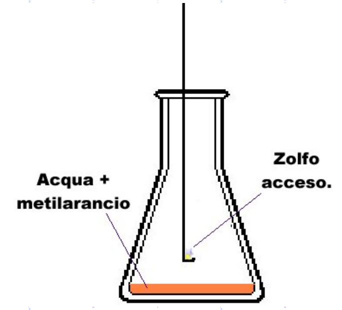
$$(result) = (y \pm U)(units)$$

where the reported uncertainty is calculated using a coverage factor of .... which gives a level of confidence of approximately ....%.

Summary of procedure for evaluating and expressing uncertainty

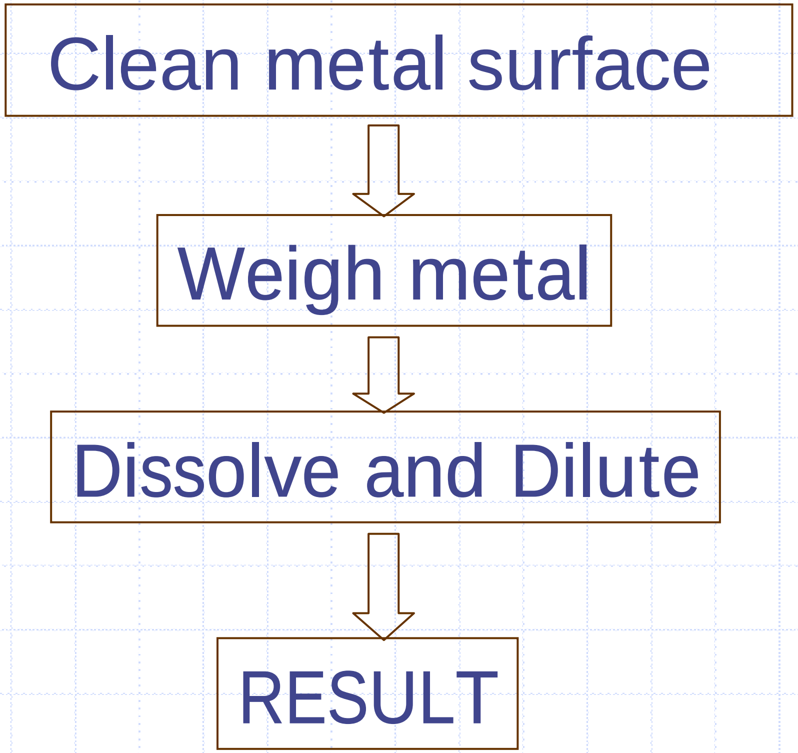
- express the relationship between the measurand Y and the input quantities X_i on which Y depends
- evaluate the standard uncertainty u (x_i) of each input estimate x_i (type A and type B)
- determine the combined standard uncertainty $u_c(y)$ of the measurement result y from the standard uncertainties and covariances associated with the input estimates
- select the coverage factor k on the basis of the level of confidence required of the interval, multiply the combined standard uncertainty by the coverage factor, tipically in the range 2 to 3, to obtain the expanded uncertainty
- report the result of the measurement together with its combined standard uncertainty $u_c(y)$ or expanded uncertainty U with its level of confidence.

Example (EURACHEM / CITAC Guide CG4 Quantify Uncertainty in Analytical Measurement)



Preparation of a calibration standard from the corrisponding high purity metal

Measurement procedure

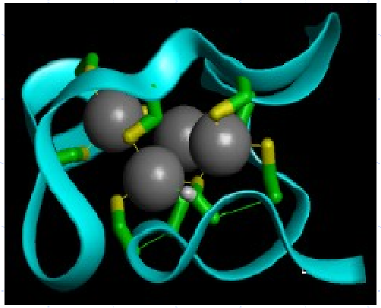


Clean metal surface

Weigh metal

Dissolve and Dilute

RESULT



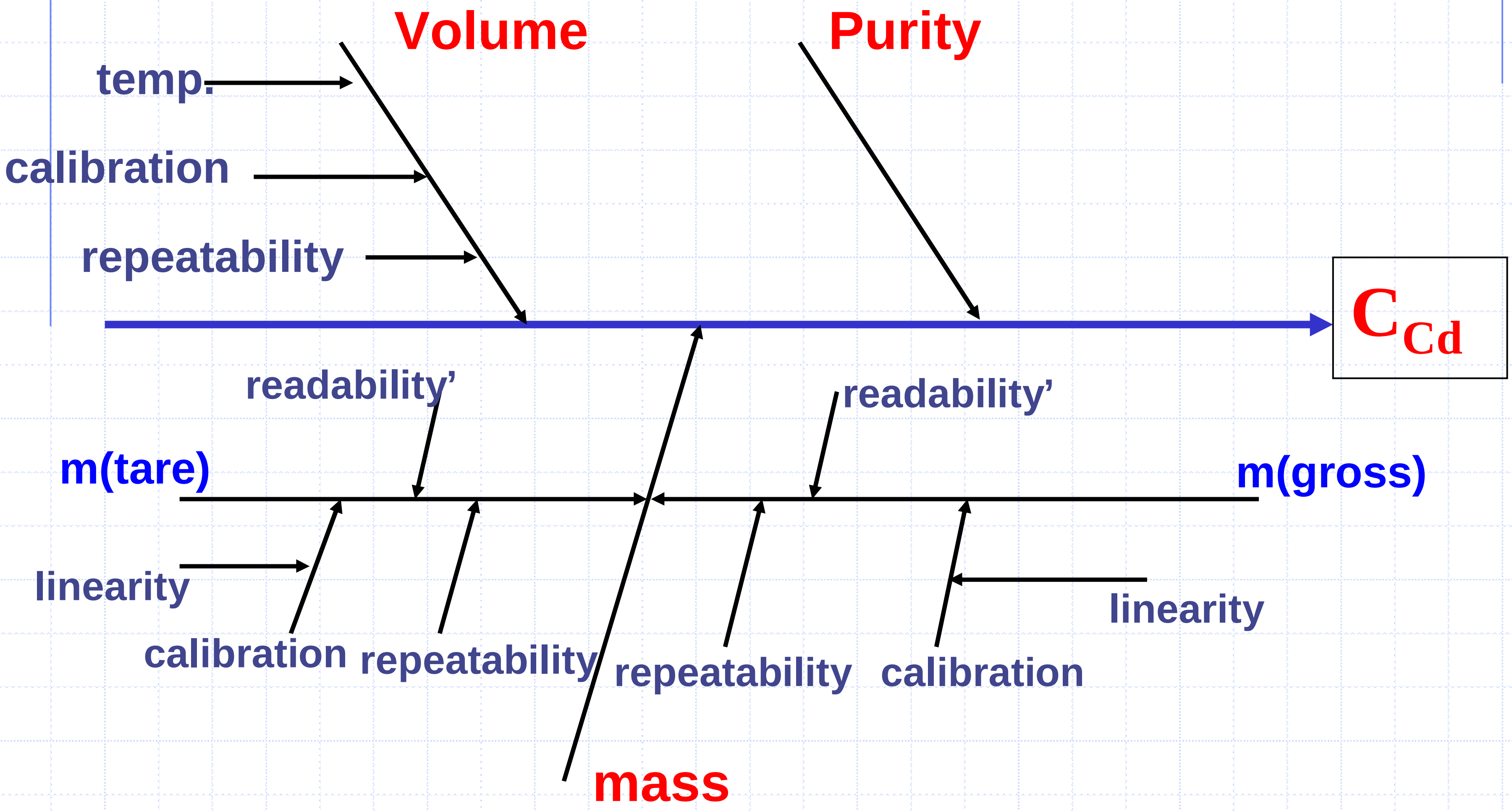
Step 1: Specification of the measurand

- The measurand is the concentration of the calibration standard solution, which depends upon the weighing of the high purity metal (Cd), its purity and the volume of the liquid in which it is dissolved.

$$C_{Cd}\left(mgL^{-1}\right) = \left(1000 * m * P\right)/V$$

- c_{Cd}: concentration of the calibration standard [mg L^{-1}]
- 1000: conversion factor from [mL] to [L]
- *m*: mass of the high purity metal
- *P*: purity of the metal given as mass fraction
- *V*: volume of the liquid of the calibration standard [mL]

Step 2: Identifying and analysing uncertainty sources



Step 3: Quantifying the uncertainty components

- **Purity *P:*** it is given on the certificate as 0.9999 ± 0.0001. Because there is no additional information about the uncertainty value, a rectangular distribution is assumed

  $P = 0.9999$

  $u(P) = 0.0001/\sqrt{3} = 0.000058$
- **Mass *m:*** the uncertainty is estimated using the data from the calibration certificate and the manifacturer's recommendations on uncertainty estimation

  $m = 100.28$ mg

  $u(m) = 0.05$ mg.
- **Volume *V*:** the volume has 3 major influences: calibration (0.04 mL), repeatability (0.02 mL) e temperature (0.05 mL)

  $V = 100.00$ mL

  $u(V) = 0.07$ mL

Step 4: Calculating the combined standard uncertainty

$$\boxed{C_{Cd}\left(mgL^{-1}\right) = \left(1000 * m * P\right)/V}$$

$$C_{Cd} = \frac{1000 * 100.28 * 0.9999}{100.0} = 1002.7 mgL^{-1}$$ Eq.1

$$\frac{u_c\left(C_{Cd}\right)}{C_{Cd}} = \sqrt{\left(\frac{u(P)}{P}\right)^2 + \left(\frac{u(m)}{m}\right)^2 + \left(\frac{u(V)}{V}\right)^2} = 0.0009$$ Eq.2

Step 4: Calculating the combined standard uncertainty

$$u_c(C_{Cd}) = \frac{u_c(C_{Cd})}{C_{Cd}} * C_{Cd} = 0.0009 * 1002.7 mgL^{-1} = 0.9 mgL^{-1}$$ Eq.3

$$U(C_{Cd}) = 2 * u_c(C_{Cd}) = 1.8 mgL^{-1}$$ Eq.4

Result

$$C_{Cd} = (1002.7 \pm 1.8) mgL^{-1}$$

GUM approach

ADVANTAGES:

- It is applicable to all kinds of measurements and to all types of input data used in measurements
- It takes into account all the sources of uncertainties

DISADVANTAGES:

- Sometime, it is complex to apply
- There is a risk of overestimate the uncertainty

Conclusion

Every time a measurement is made, there is some uncertainty about the result

No measurement is ever guaranteed to be perfect

Uncertainty of measurement is the doubt that exists about the result of any measurement

By quantifying the possible spread of measurements, we can say how confident we are about the result

THANK YOU

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