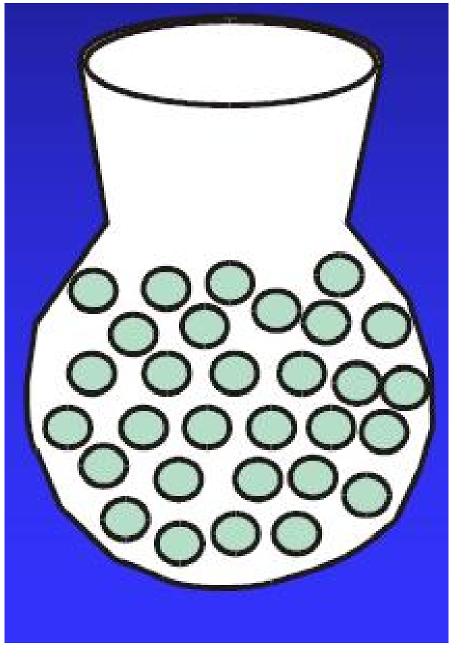
Why do we have Measurement Uncertainty?

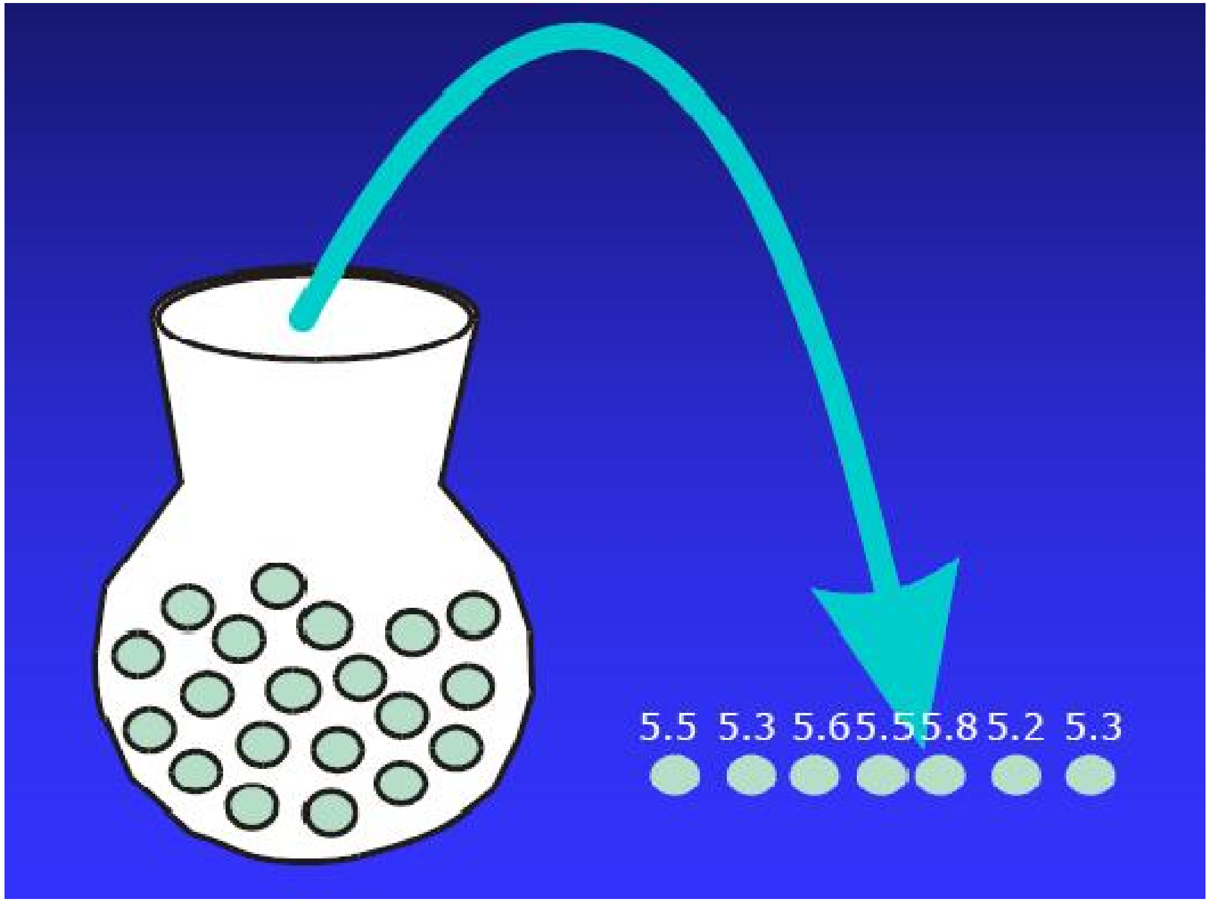
Measurement Uncertainty

- Content

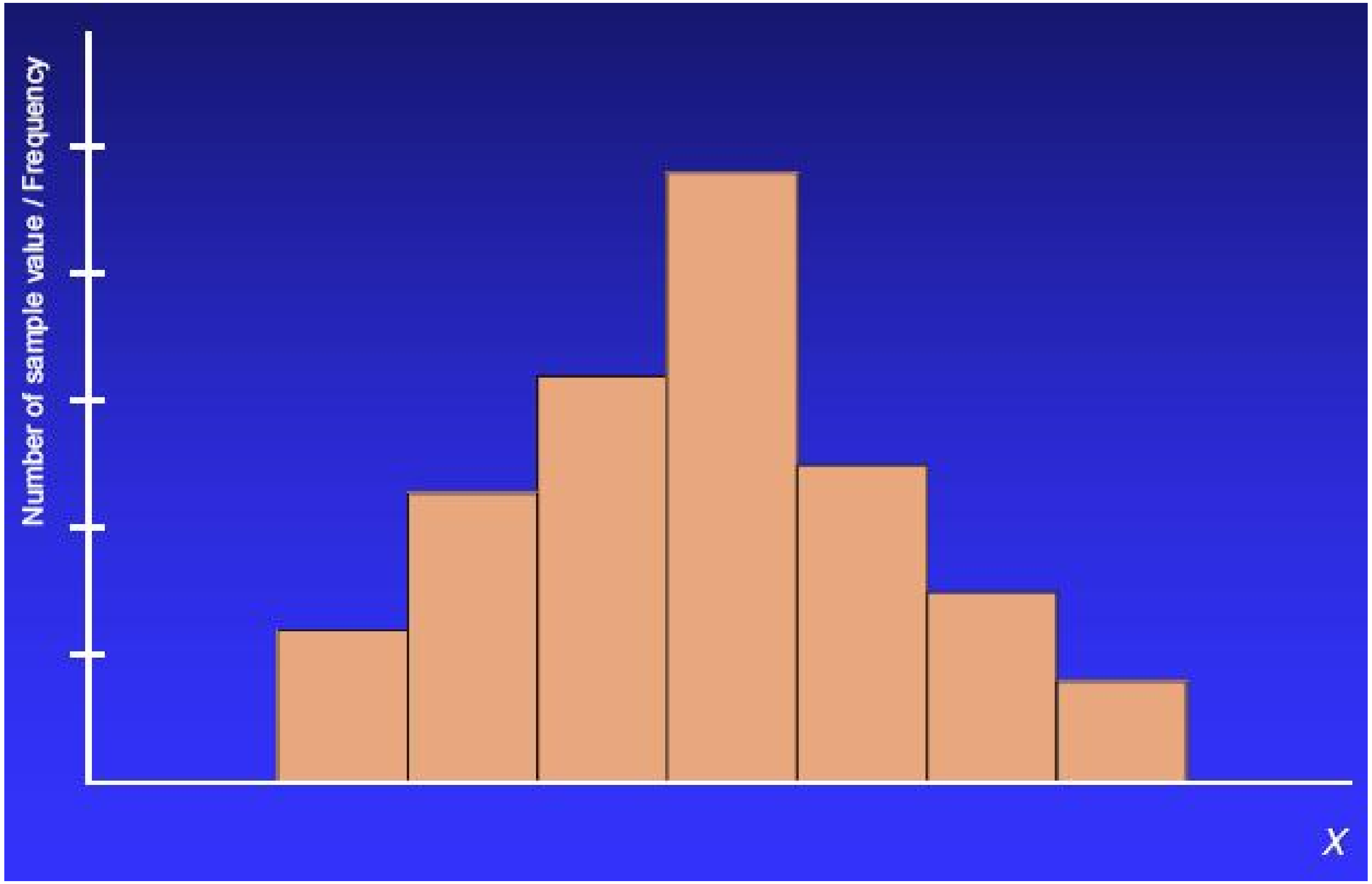
Model of the Measurement Process



Model of the Measurement Process



Random Effects



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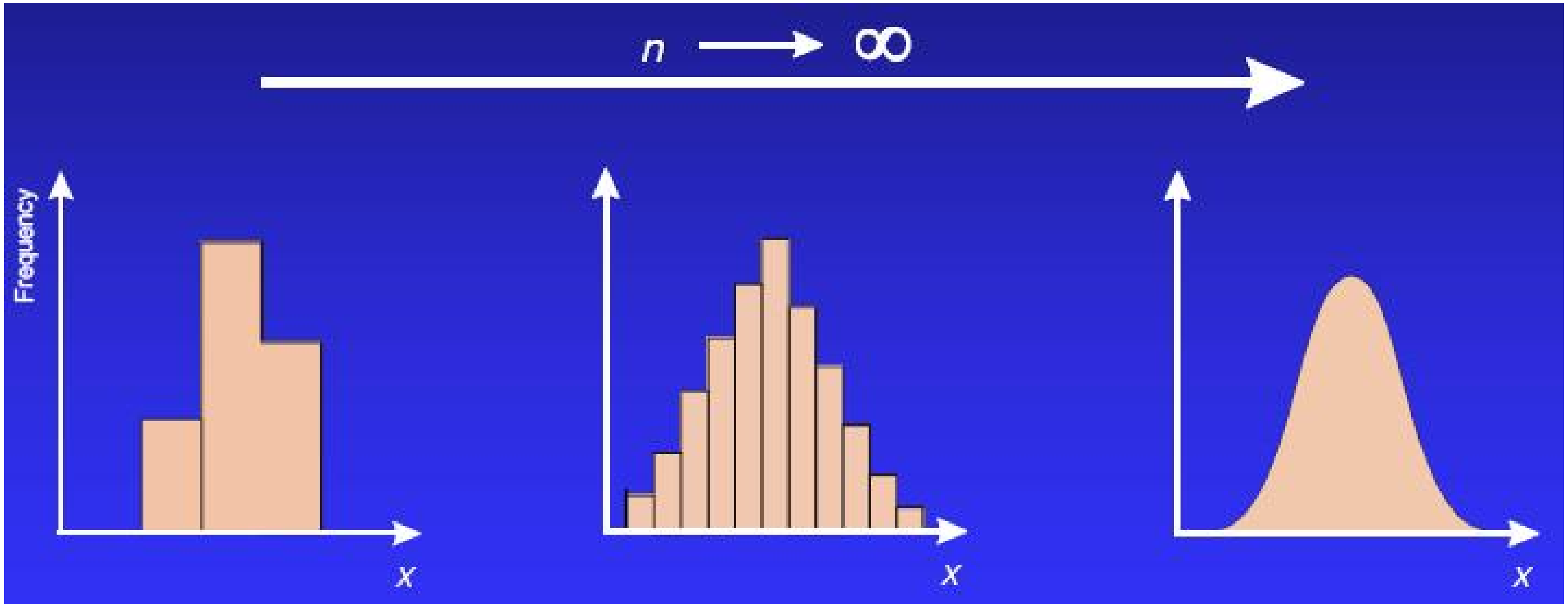

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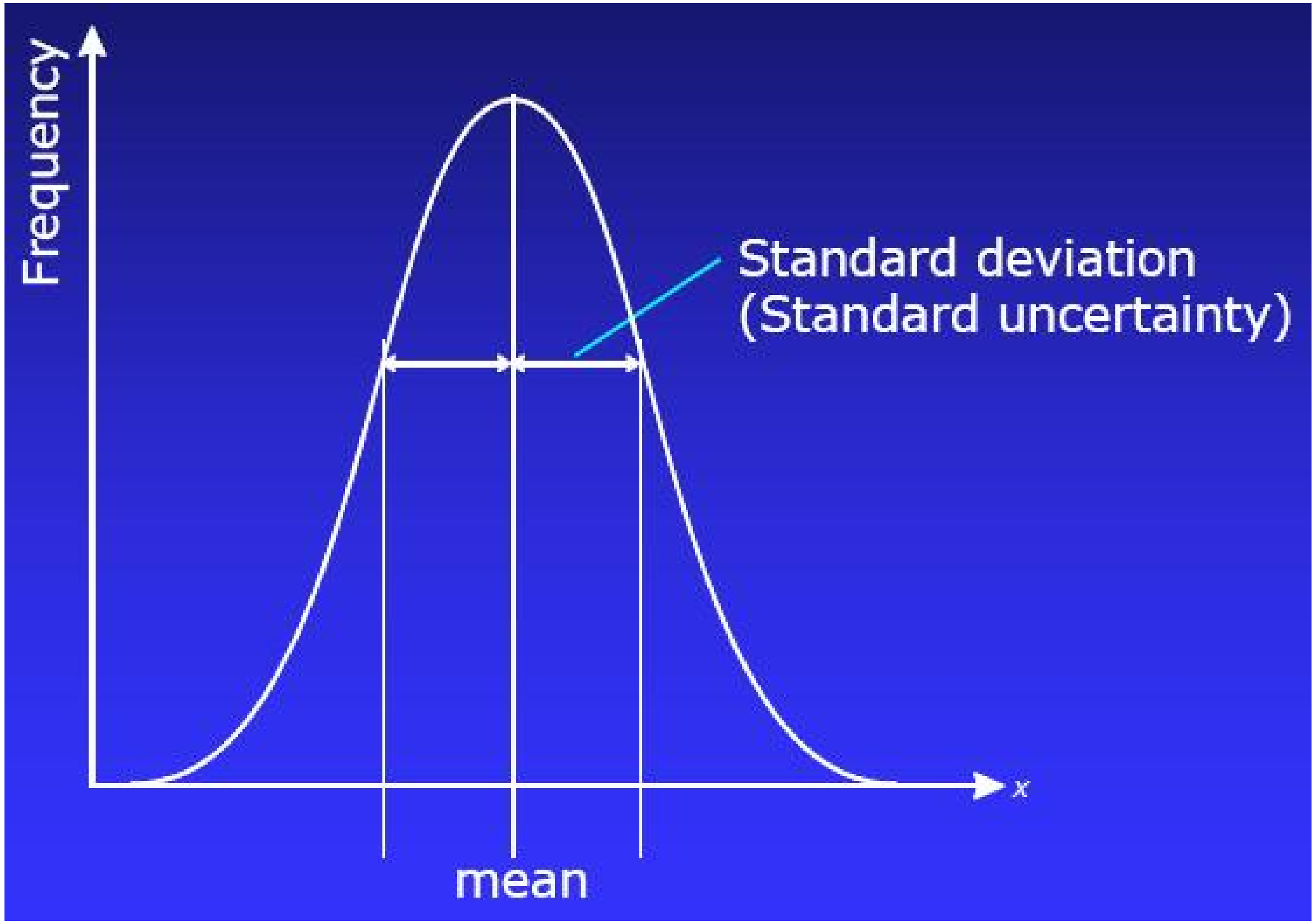


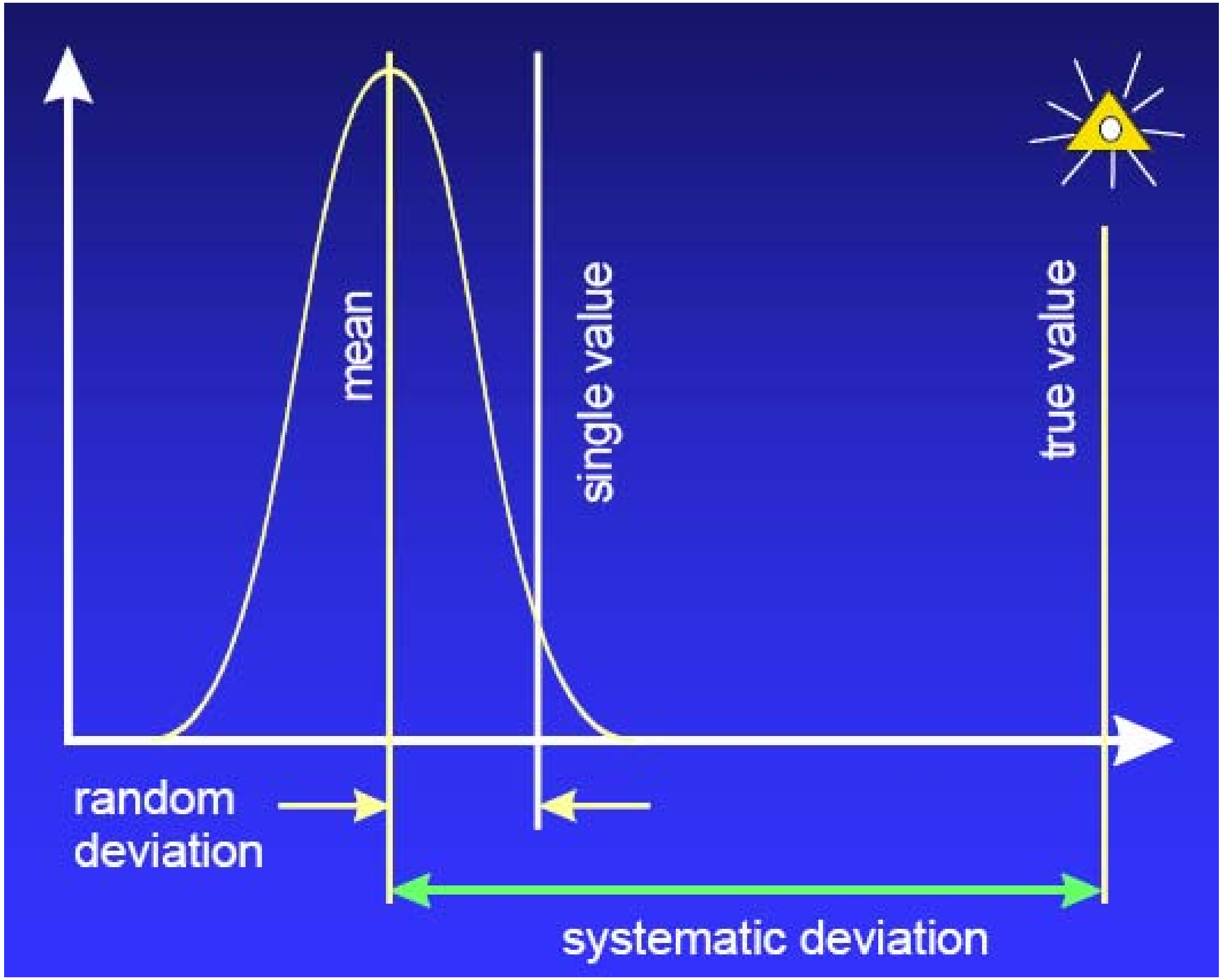
Random Effects

- Mean: $$\bar{x} = \frac{x_1 + x_2 + \ldots + x_i + \ldots + x_n}{n} = \frac{\sum_{i=1}^{n} x_i}{n}$$

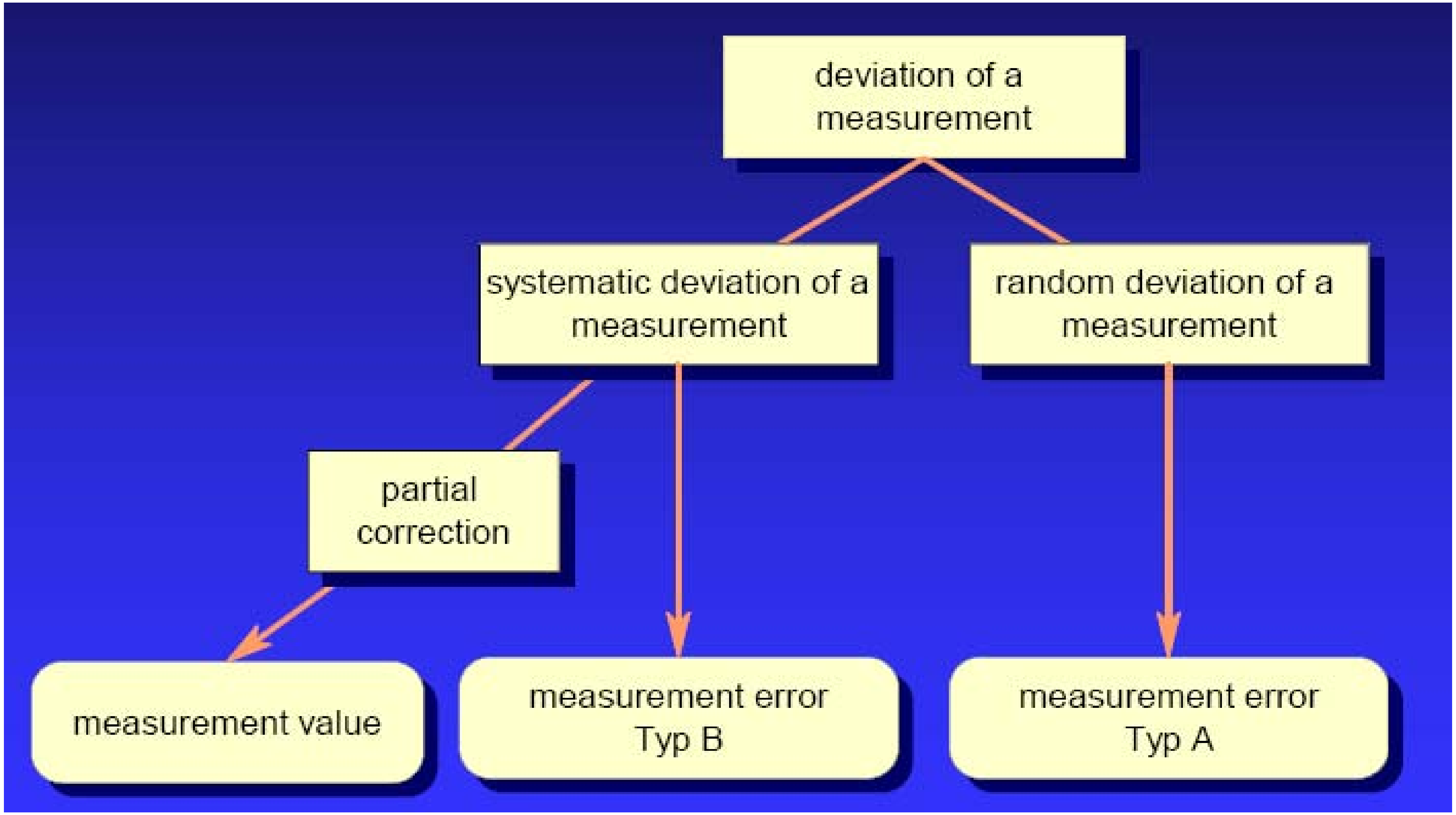
- Standard deviation:

$$s = \sqrt{\frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + \ldots (x_n - \bar{x})^2}{n-1}} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}}$$

Systematic Effects



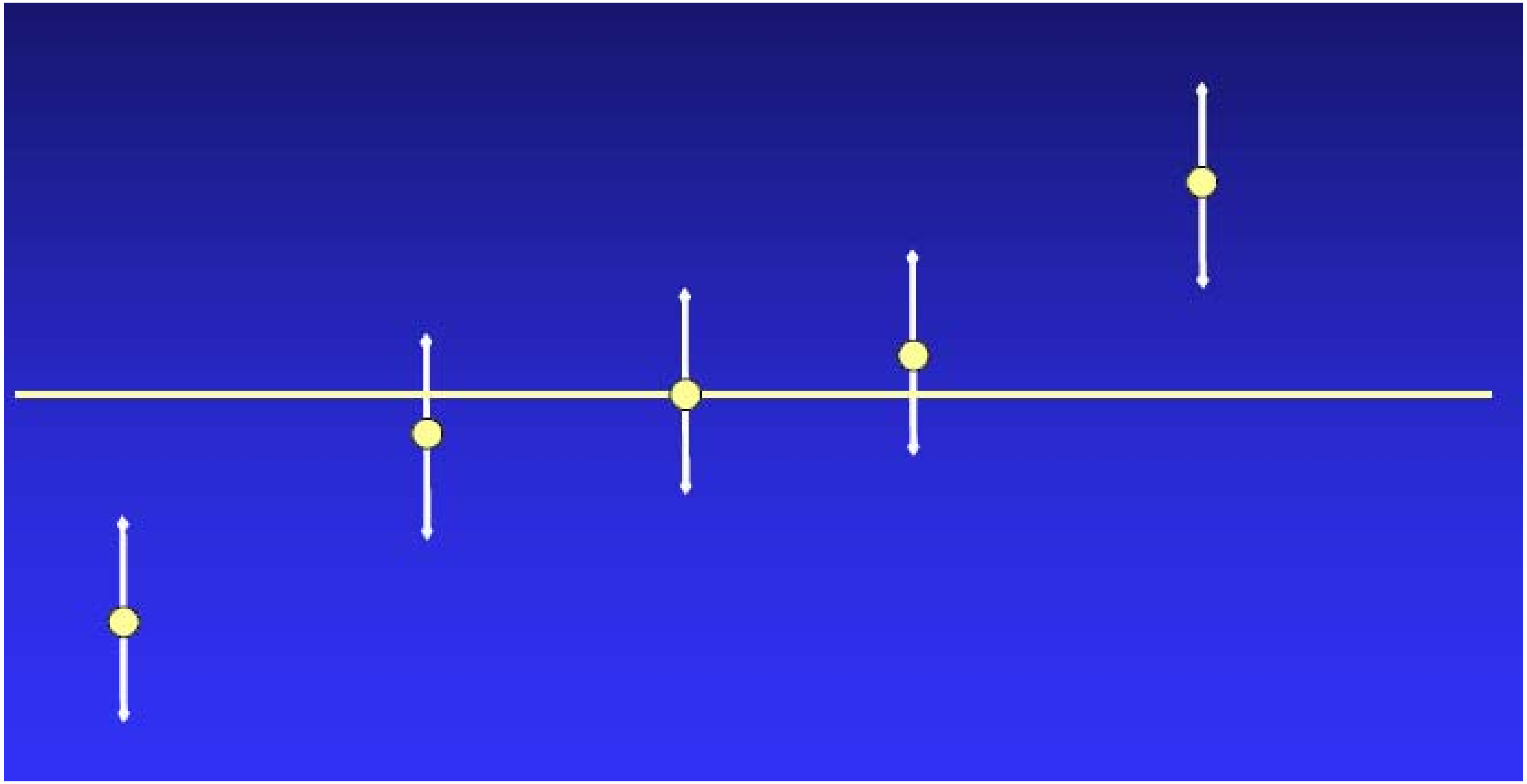
Random and Systematic Deviations as Error Type A and Type B



Major Goals

- Comparabilitiy of Measurement Results
- Easy defintion of determination the Uncertainty

Comparing Results



History

- 1993 Guide to the Expression of Uncertainty in Measurement (ISO)
- 1995 Quantifying Uncertainty in Analytical Measurement (Eurachem/CITAC)
- 2000 Quantifying Uncertainty in Analytical Measurement Second Edition (Eurachem/CITAC Guide)

Uncertainty

- Is a fundamental property of a result
- It is not an optional extra
- It is not just as an additional burden
- All results have an uncertainty on their value
- Needs to be evaluated irrespective of requirements of 17025

Overview

- What is meant by Uncertainty?
- What information is it intended to give?
- Why is it important?
- How is uncertainty evaluated?

What is Uncertainty ?

- There will always be an uncertainty about the value of a result
- Even when correction factors have been applied
- Because there will be an uncertainty on these factors
- There will also be an uncertainty arising from random effects

Why Uncertainty is Important ?

- 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

Uncertainty should be quantified in a Way that is

- **Universal**:

  applicable to all kinds of measurements

- **Internally consistent**:

  independent of how components are grouped

- **Transferable**:

  use uncertainty on a result in derivation of uncertainty on dependent results

- **Procedures set out in**:

  CITAC Guide to the Expression of Uncertainty in Measurements (GUM)

Uncertainty of Measurement - Definition

Parameter,

- associated with the result of a measurement,
- that characterizes the dispersion of the values
  that could reasonably be attributed to the measurand

Definition of uncertainty

Uncertainty of measurement comprises, in general, many components.

- Some of these components may be evaluated from the statistical distribution of the results of series of measurements and can be characterised by standard deviations.

- The other components, which also can be characterised by standard deviations,
  - are evaluated from assumed probability distributions based on experience
  - or other information.

Uncertainty sources

In practice the uncertainty on the result may arise from many possible sources, e.g.:

- sampling,
- matrix effects and interferences,
- environmental conditions,
- uncertainties of weights and volumetric equipment,
- reference values.

Evaluating Uncertainty
Sources of uncertainty

1. Incomplete definition of the measurand.
2. Sampling – the sample measured may not be representative.
3. Incomplete implementation of the measurement method.
4. Personal bias in reading analouge instruments.

Evaluating Uncertainty
Sources of uncertainty

5. Inadaquate knowledge

- of the effects of environmental conditions on the measurement procedure
- or imperfect measurement of environmental conditions.

6. Instrument calibration uncertainty.

7. Instrument resolution or discrimination threshold.

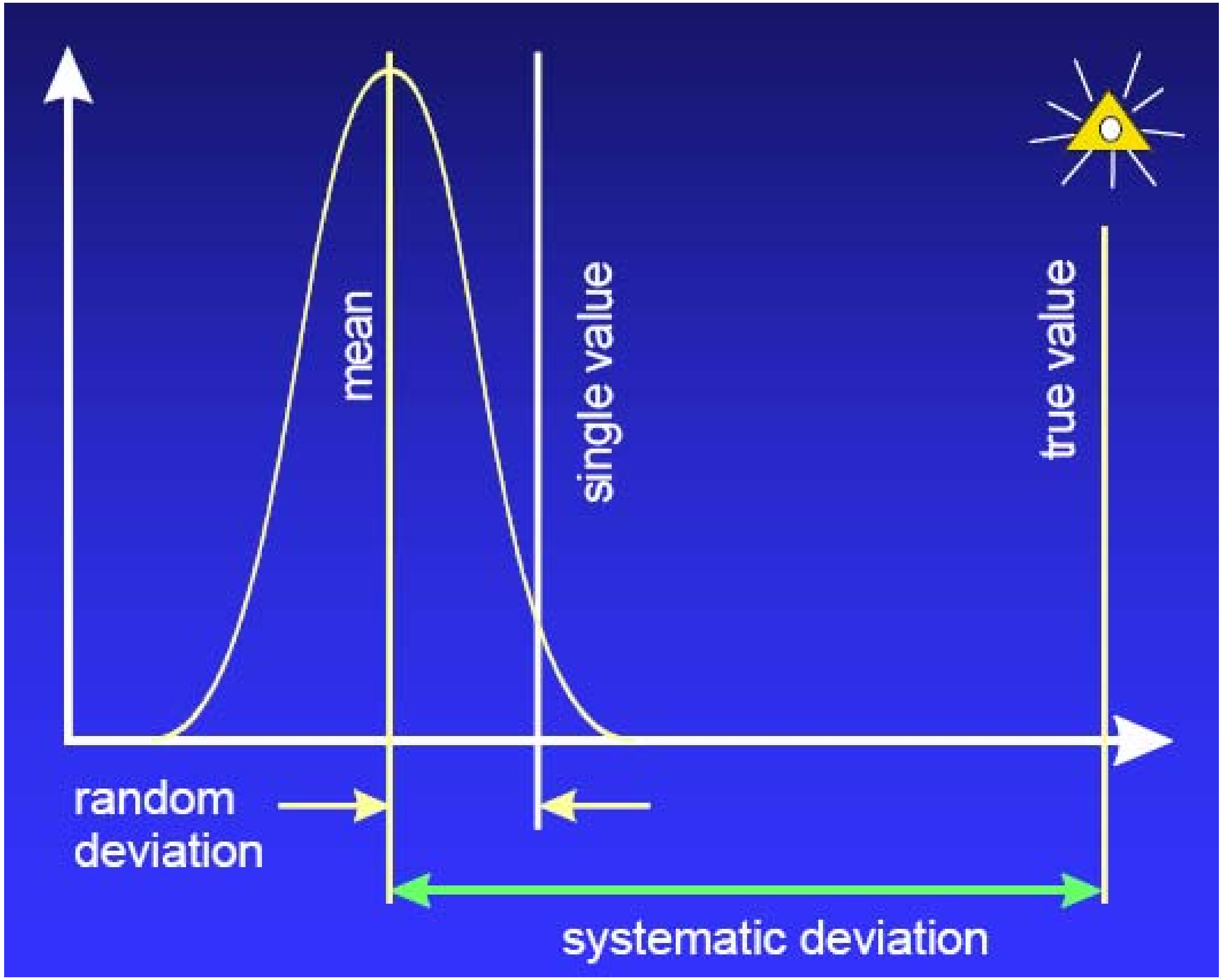
Error and uncertainty

The uncertainty of the result of a measurement should never be interpreted as representing the error itself, nor the error remaining after correction.

An error is regarded as having two components, namely,

- a random component and
- a systematic component.

Systematic Effects



Error and uncertainty

Random error

typically arises from unpredictable variations of influence quantities.

These random effects give rise to variations in repeated observations of the measurand.

The random error of an analytical result

- cannot be compensated by correction
- but it can usually be reduced by increasing the number of observations.

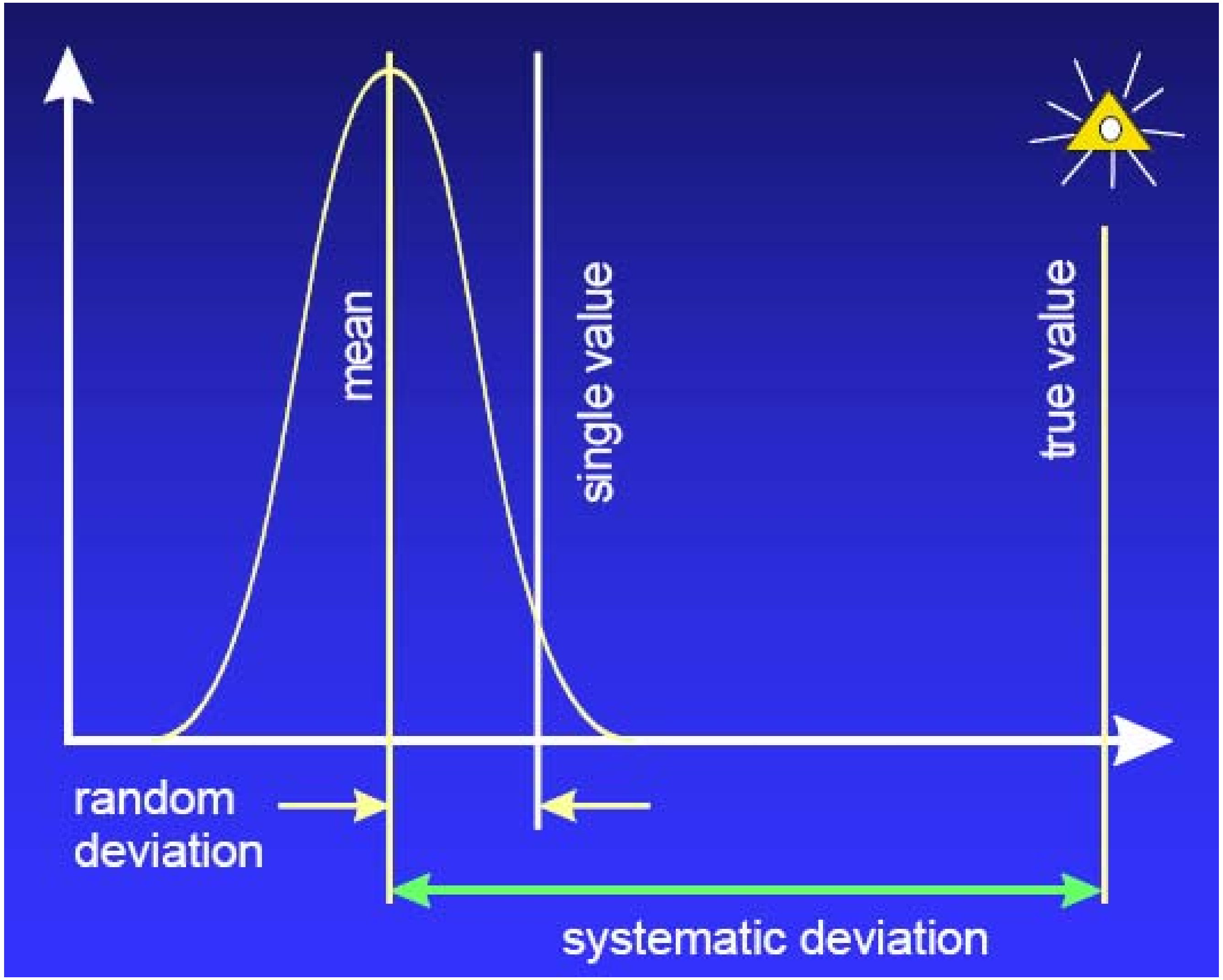
Error and uncertainty

Systematic error

is defined as a component of error which, in the course of a number of analyses of the same measurand, remains constant or varies in a predictable way.

- It is independent of the number of measurements made and
- cannot therefore be reduced by increasing the number of analyses under constant measurement conditions.

Systematic Effects



The process of measurement uncertainty estimation

step 1: specify measurand

step 2: identify uncertainty sources

step 3: quantify uncertainty components

step 4: calculate combined uncertainty

The process of measurement uncertainty estimation

step 1 specify measurand

Write down 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.*) upon which it depends.

Where possible, include corrections for known systematic effects.

The specification information should be given in the relevant Standard Operating Procedure (SOP) or other method description.

The process of measurement uncertainty estimation

step 2 identify uncertainty sources

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.

The process of measurement uncertainty estimation

step 3 quantify uncertainty components

Measure or estimate the size of the uncertainty component associated with each potential source of uncertainty identified.

It is also important

- to consider whether available data accounts sufficiently for all sources of uncertainty,
- and plan additional experiments and studies carefully to ensure that all sources of uncertainty are adequately accounted for.

The process of measurement uncertainty estimation

step 4 calculate combined uncertainty

The information obtained in step 3 will consist of a number of quantified contributions to overall uncertainty,

- whether associated with individual sources
- or with the combined effects of several sources.

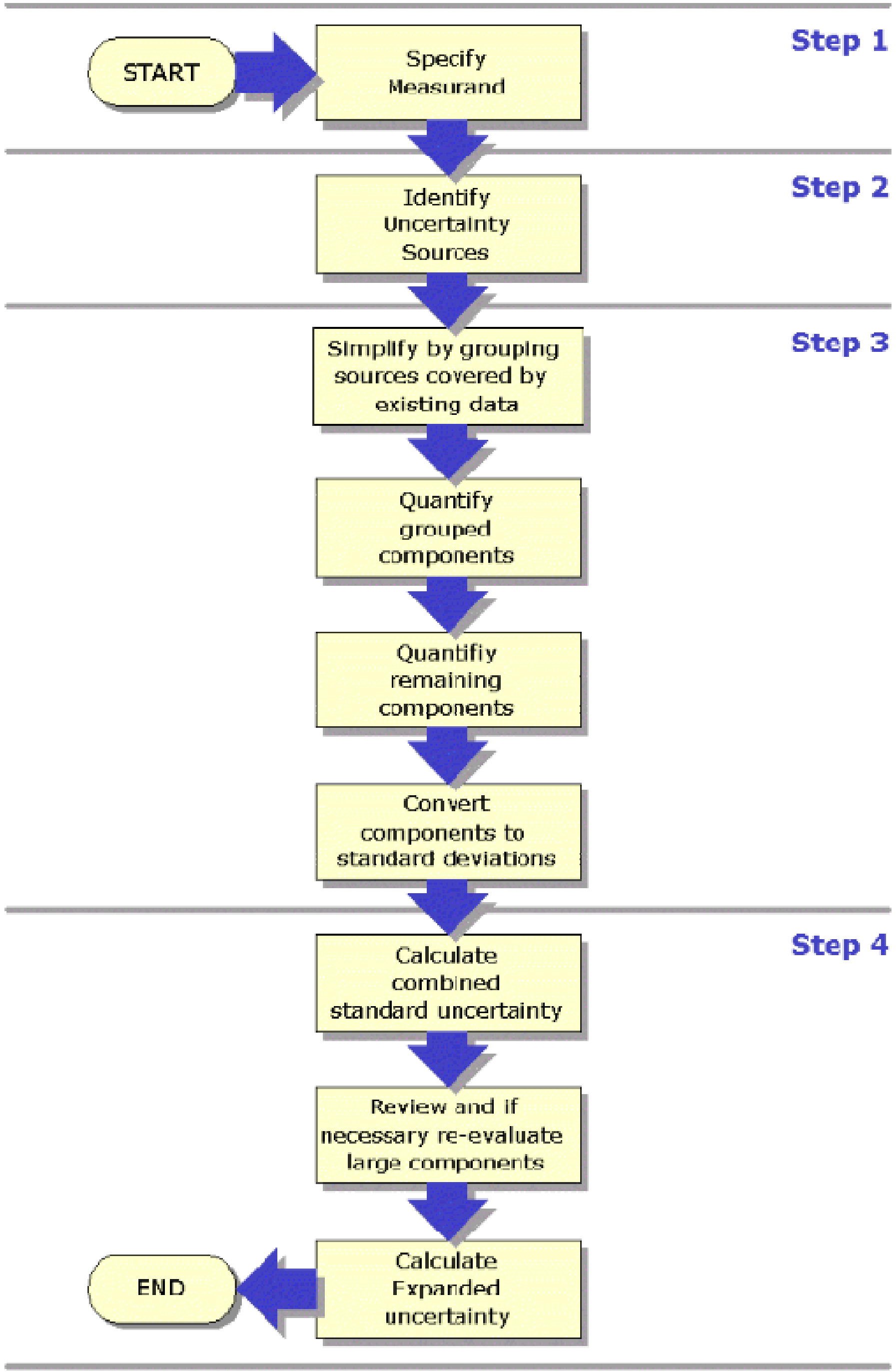
The contributions have

- to be expressed as standard deviations,
- and combined according to the appropriate rules,

to give a combined standard uncertainty.

The appropriate coverage factor should be applied to give an expanded uncertainty.

The process of measurement uncertainty estimation



Conclusions

- Uncertainty is an essential component of the result.
- Necessary to ensure comparability of results.
- In many cases method validation studies & QA data provide most of information required.
- More information on:

www.measurementuncertainty.org

Rules for Calculation

1.Rule: Addition and Substraction

$$y = k(p + q - r + ...)$$

$$u_c(y(p,q,r,...)) = k * \sqrt{u(p)^2 + u(q)^2 + u(r)^2 + ...}$$

Rules for Calculation

2. Rule: Multiplication and Division

$$y = k(p * q * ...)$$

$$u_c(y) = y * k * \sqrt{(\frac{u(p)}{\bar{p}})^2 + (\frac{u(q)}{\bar{q}})^2 + ...}$$