Uncertainty of Measurement (Analytical)

Maré Linsky

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Uncertainty of Measurement (Analytical)

- ✓ Introduction
  - ✓ Concepts and definitions
- ✓ GUM (Guide to the Expression of Uncertainty in Measurement)
- ✓ Method Validation and Quality Control
- ✓ Uncertainty Estimation using method validation and quality control data (Nordtest Guide)

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What is a measurement?

- A set of operations to determine the value of a quantity.
  - Measurements are made using a measuring instrument.
  - It tells us about a property of a thing.
  - The result of a measurement has two parts:
    - Number
    - Unit … Uncertainty

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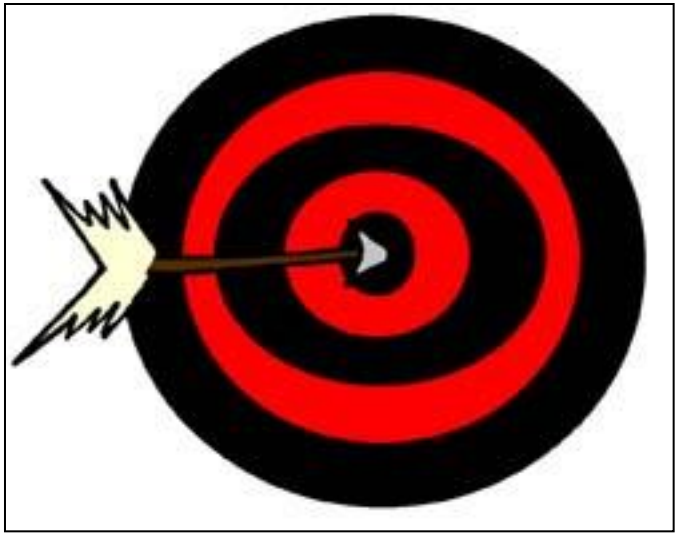
Accuracy (ISO 3534)

Closeness of agreement between a test result or measurement result and the true value.



True value (VIM 3)

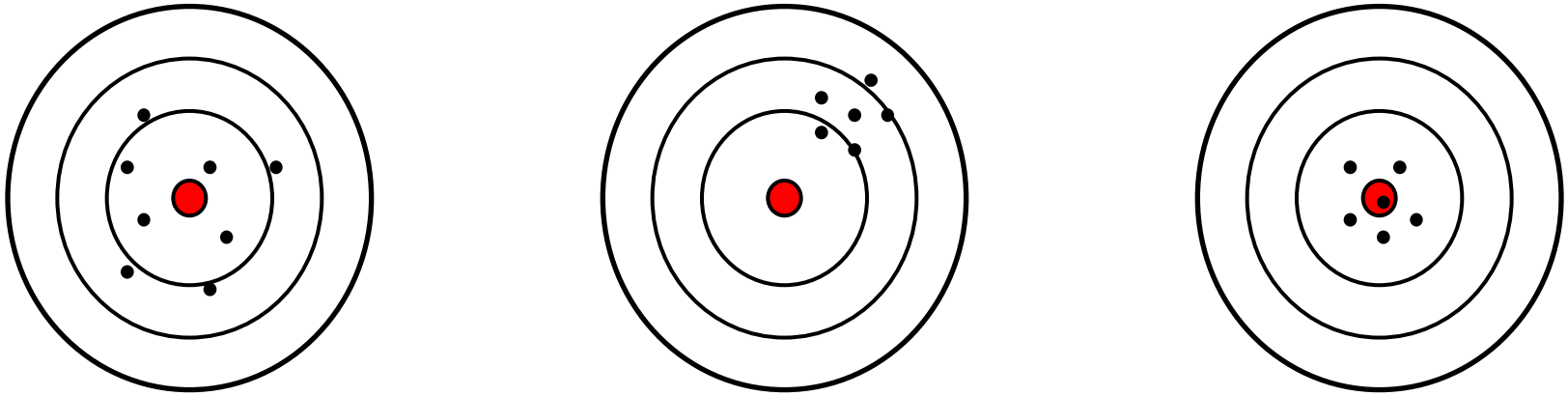
Quantity value consistent with the definition of a quantity.

Conventional true value

A value attributed to a particular quantity and accepted, sometimes by convention, as having an uncertainty appropriate for a given purpose.

Precision (ISO 3534)

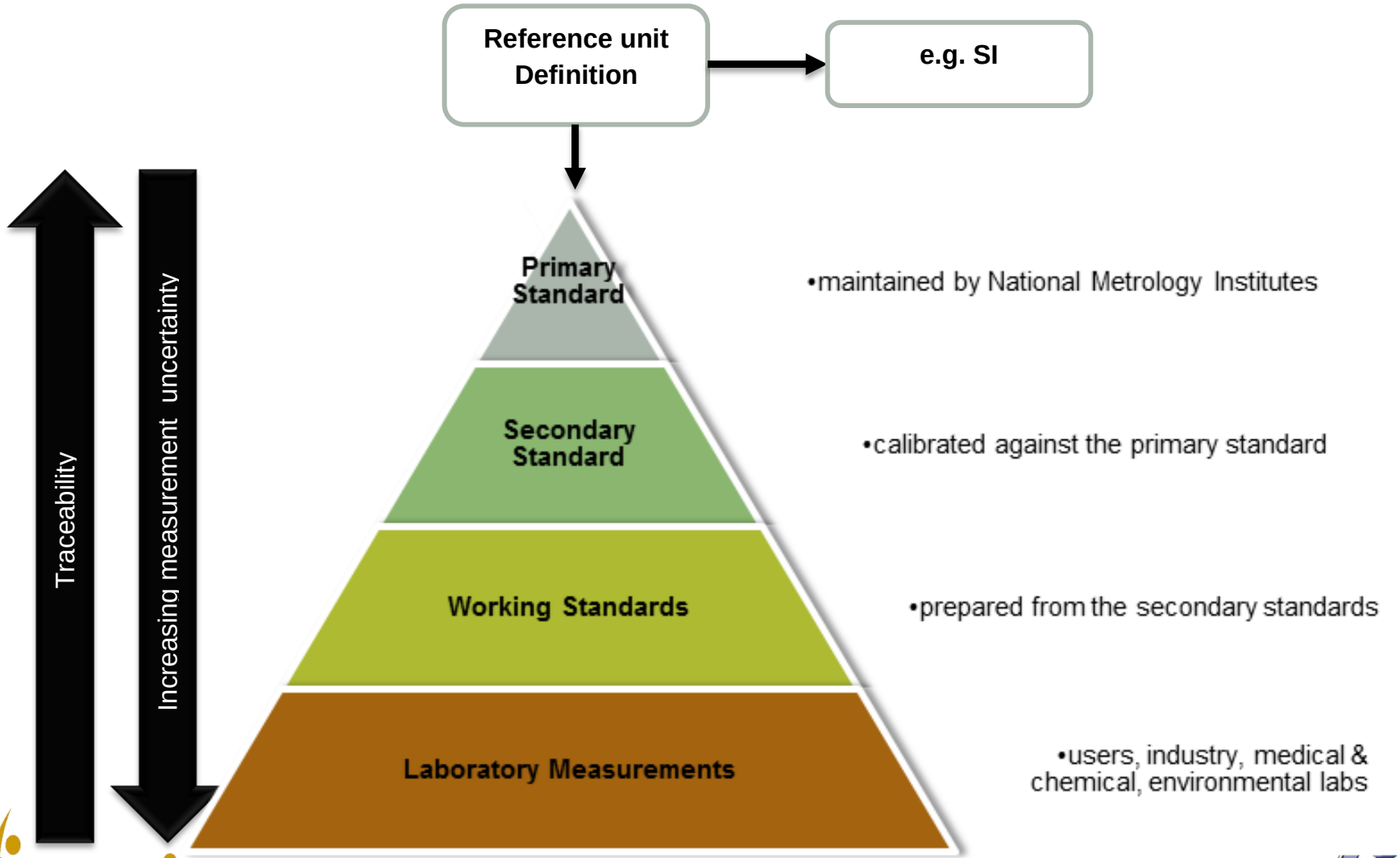
Closeness of agreement between independent test / measurement results obtained under stipulated conditions



Metrological traceability (VIM 3)

Result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty

Calibration hierarchy establishing measurement traceability to the reference unit



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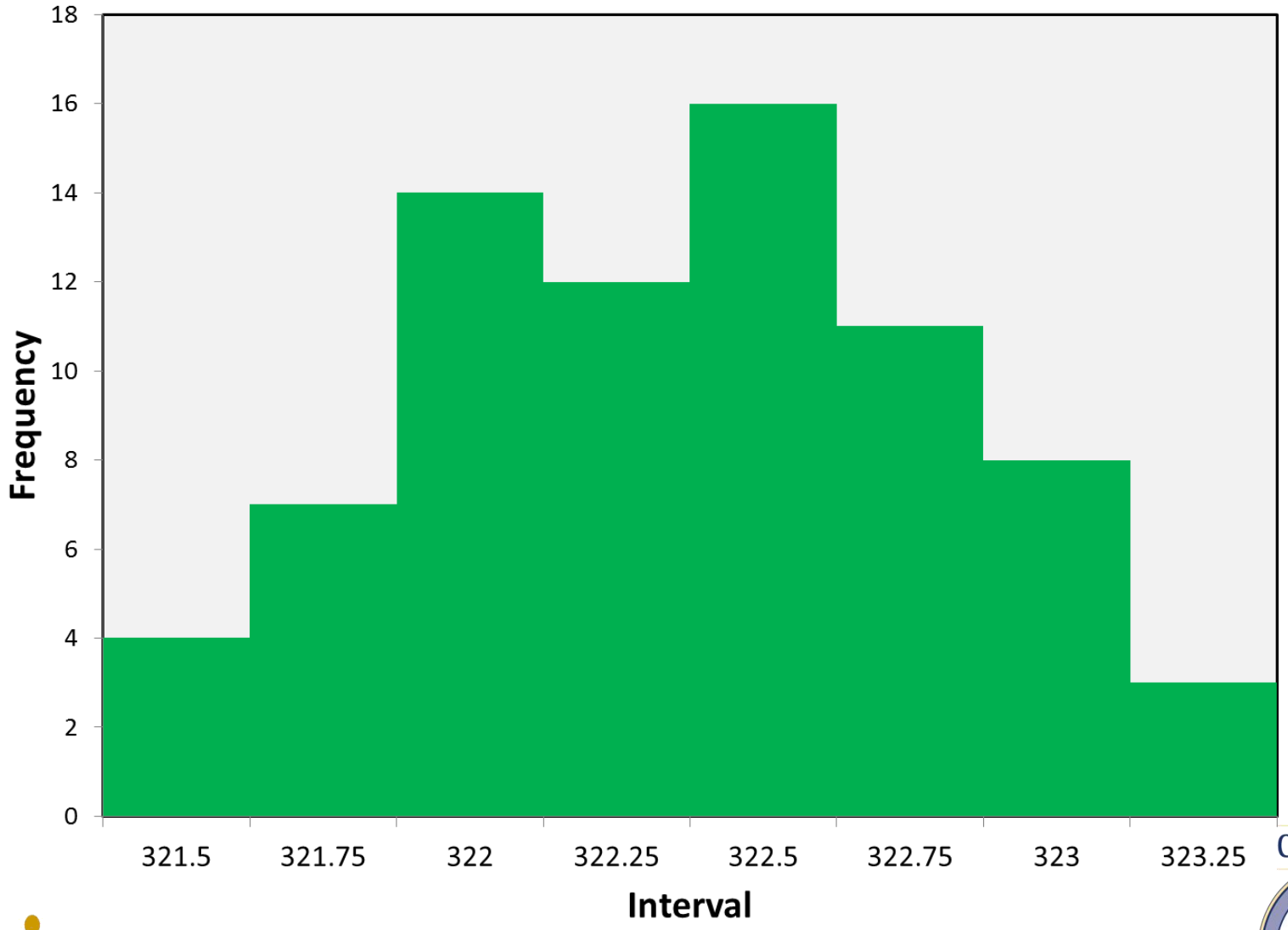
Analytical Results Vary

- ✓ Variations are always present.
- ✓ If there seems to be none, the resolution is not high enough.

322	322,3	322,29
322	322,5	322,49
322	322,3	322,28
322	322,2	322,17
322	321,7	321,67
322	321,8	321,76
322	321,7	321,75
322	322,2	322,17
322	321,6	321,58
322	322,4	322,36
322	322,4	322,40

Histogram



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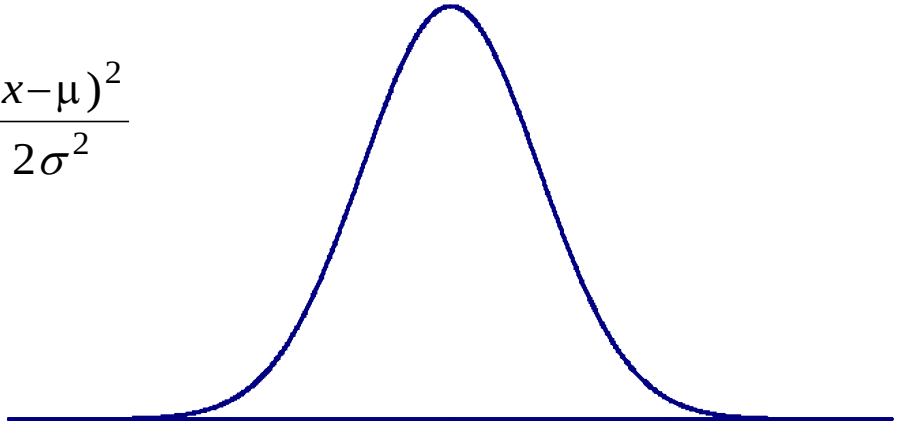
Normal Distribution

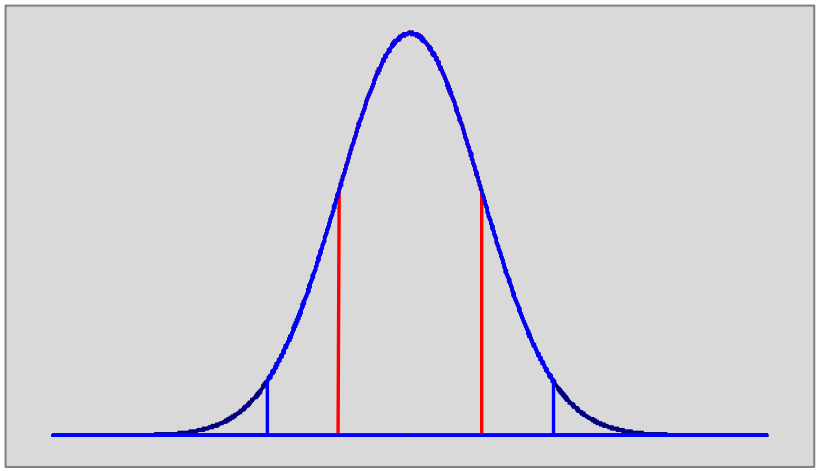
- Bell shaped
- Completely determined by μ and σ
- The curve is symmetrical about μ
- The greater the value of σ the greater the spread of the curve

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



Normal Distribution: Important Properties

- ✓ Approximately 68% (68,27%) of the data lie within $\mu \pm 1\sigma$
- ✓ Approximately 95 % (95,45%) of the data lie within $\mu \pm 2\sigma$
- ✓ Approximately 99,7 % (99,73%) of the data lie within $\mu \pm 3\sigma$



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Confidence Limits / Intervals

- ✓ The confidence limits describe the range within which we expect with given confidence the true value to lie.

Uncertainty of measurement

Parameter, associated with the result of a measurement, that characterises the spread of values that could reasonably be attributed to the measurand (GUM).

OR

Non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used (VIM 3).

What is uncertainty of measurement?

- It tells us something about the quality of the measurement i.e. how much you can trust the measurement.
- We need two numbers to quantify uncertainty:
  - The width of the margin of doubt, the confidence interval, and
  - The confidence level, how sure we are that the true value is within the margin of doubt.

Basic concepts

- ✓ Standard Uncertainty

$$u(x_i) @ LOC = 68\%$$

- ✓ Combined Standard Uncertainty

$$u_c(y) = \sqrt{\sum (c_i \cdot u(x_i))^2}$$

- ✓ Expanded Uncertainty

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

  - ✓ k = Coverage factor associated with:
    - ✓ Level of Confidence
    - ✓ Degrees of Freedom

Basic concepts

- Uncertainty (of measurement)

$$Y = y \pm U$$

$$m = 1000.00250 \pm 0.00050\ g$$

- Level of Confidence
- Coverage factor
- Effective degrees of freedom

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Guide to the Expression of Uncertainty in Measurement (GUM)

Introduction

- ✓ Purpose of the GUM
  - ✓ Establish general rules and procedures for evaluating and expressing uncertainty of measurement
  - ✓ To provide a basis for international comparison of measurement results
  - ✓ Applicable to a broad spectrum of measurements at various levels of accuracy
- ✓ Bottom Up approach

Method of evaluation: Analytical measurement

- ✓ Step 1: Specification and modeling
- ✓ Step 2: Identify the uncertainty sources
- ✓ Step 3: Quantify the uncertainty sources
- ✓ Step 4: Calculate the total uncertainty (combined standard uncertainty)
- ✓ Step 5: Calculate the expanded uncertainty
- ✓ Step 6: Reporting the uncertainty

Step 1: Specification and modeling

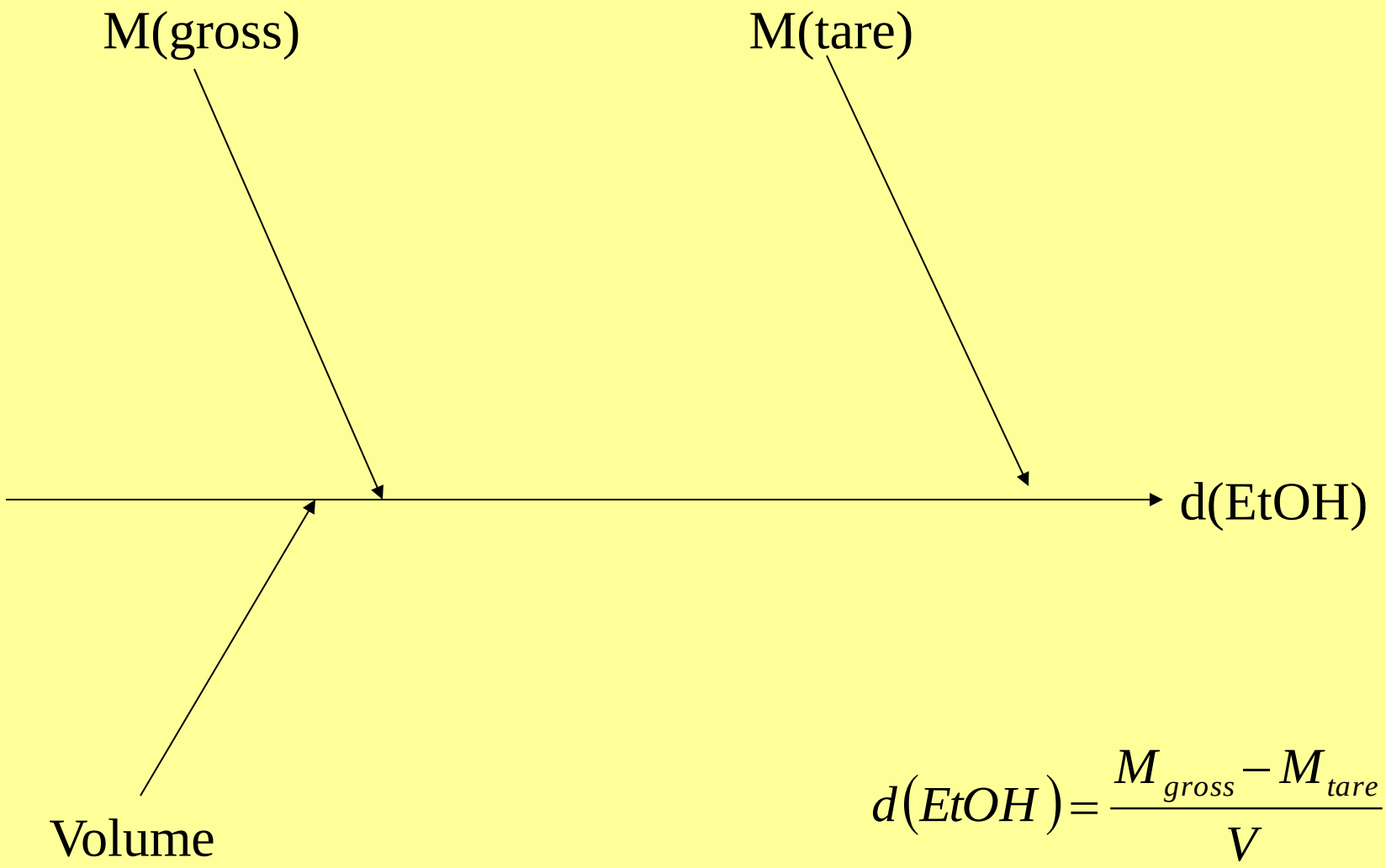
- ✓ A clear and unambiguous statement of what is being measured.
  - ✓ Measurand
  - ✓ Matrix
  - ✓ Method
- ✓ Mathematical Model

$$y = f(x_1, x_2, ..., x_N)$$

Step 2: Identify uncertainty sources

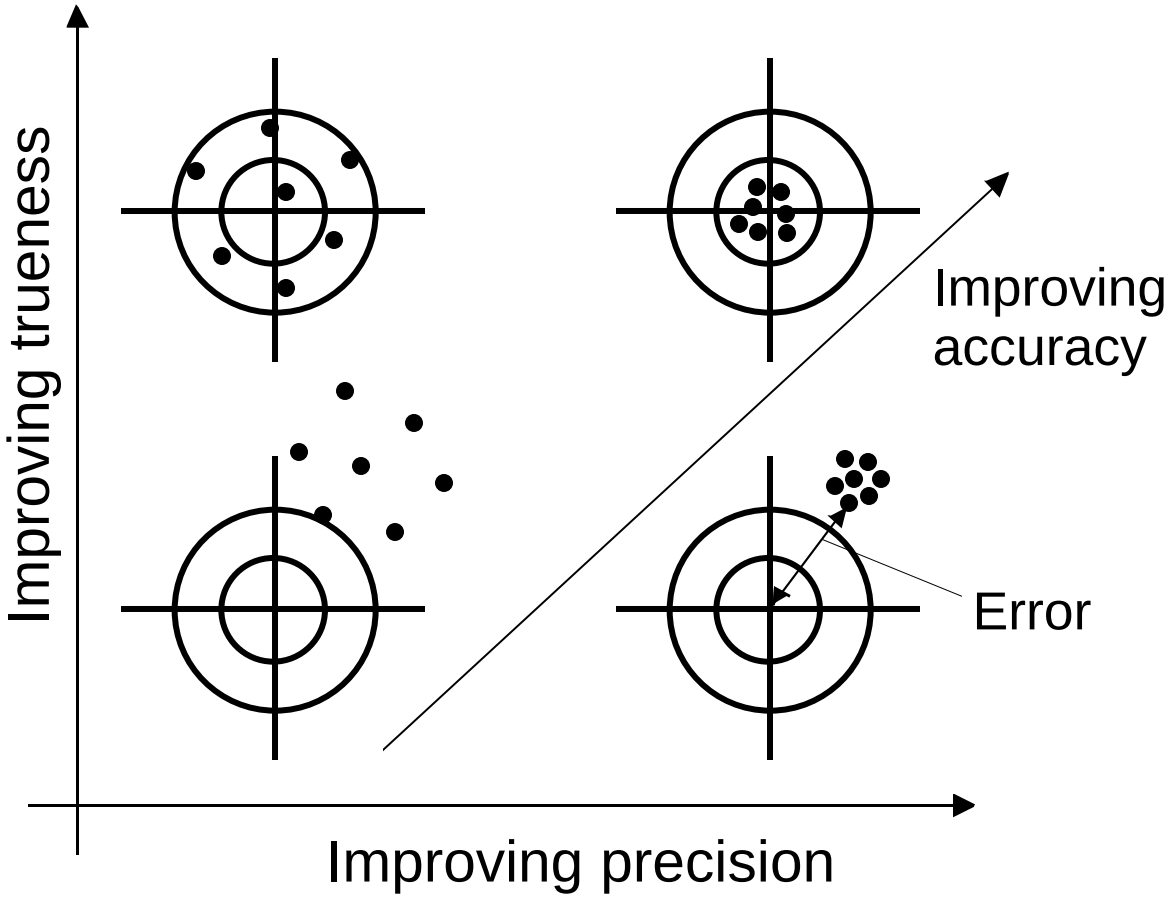
- ✓ Sampling
- ✓ Storage conditions
- ✓ Environmental conditions
- ✓ Reagent purity, blank correction
- ✓ Sample, matrix effects
- ✓ Operator effects
- ✓ Instrument effects
- ✓ Calibration Standards
- ✓ Calibration effects
- ✓ Random effects
- ✓ Constants

Step 2: Identify uncertainty sources



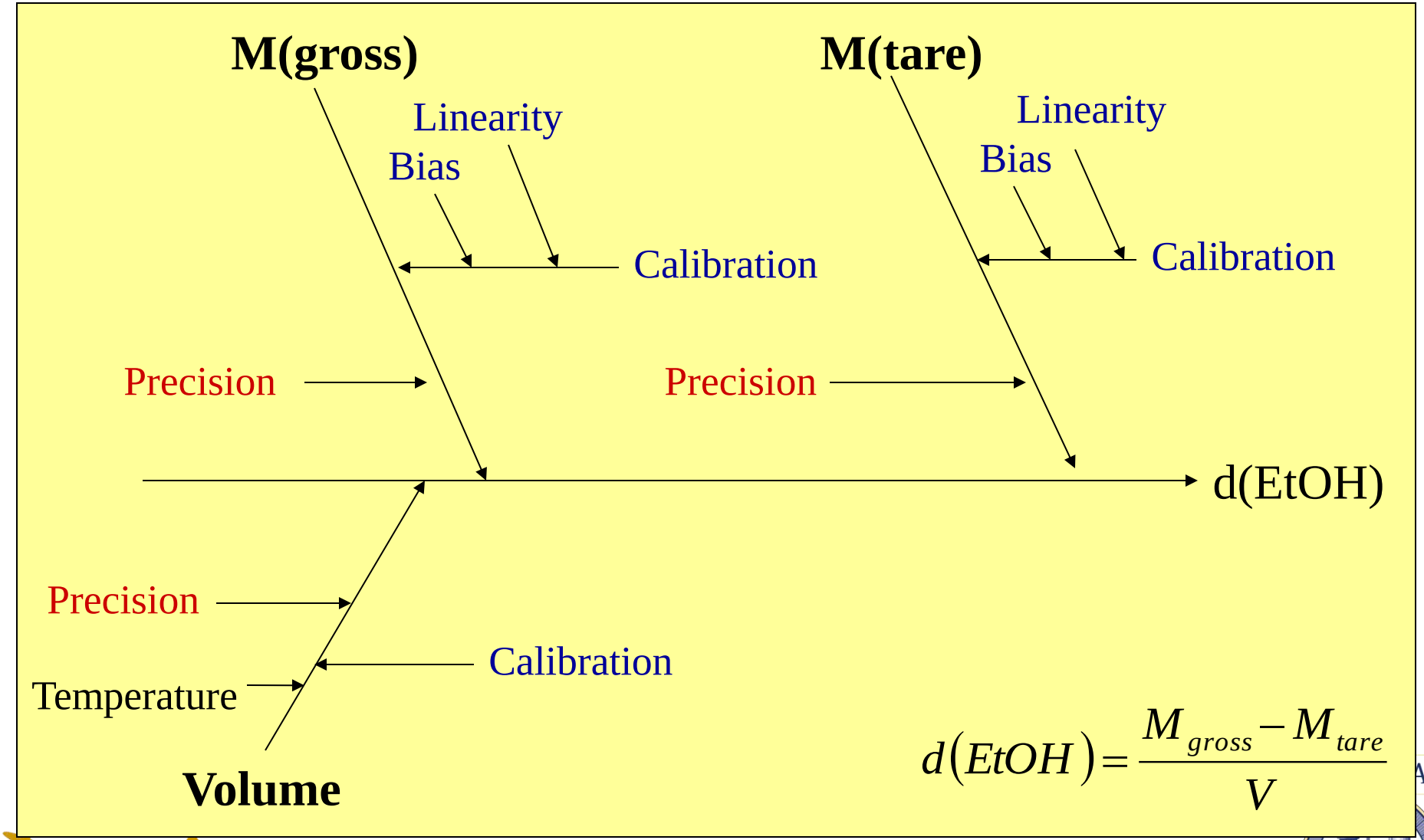
$$d(EtOH) = \frac{M_{gross} - M_{tare}}{V}$$

Accuracy, Trueness & Precision



from: LGC, vamstat II

Cause and Effect / Fishbone diagram



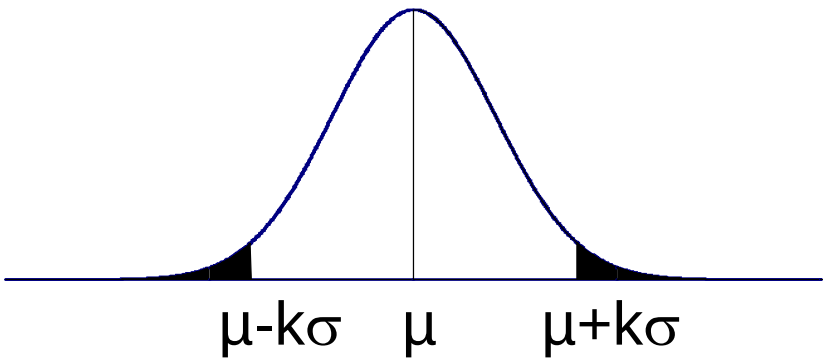
$$d(EtOH) = \frac{M_{gross} - M_{tare}}{V}$$

Step 3: Quantifying uncertainty sources

- ✓ Two categories based on method of evaluation
  - ✓ Type A: Estimate and associated uncertainty are directly determined by the current measurement (Statistics)
  - ✓ Type B: Estimate and associated uncertainty are brought into the measurement from external sources (Other sources)
- ✓ Both are based on probability distributions
  - ✓ Standard uncertainty of each input estimate is obtained from a distribution of possible values for the input quantity
  - ✓ Based on the state of our knowledge

Type A evaluation

- ✓ For component of uncertainty arising from random effects.
- ✓ Applied when multiple independent observations are made under the same (repeatability) conditions.
- ✓ Usually obtained from a normal (Gaussian) probability density function



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Type A evaluation

- ✓ Best estimate of the expected value of an input quantity: Arithmetic mean

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$$

- ✓ Distribution of the quantity: Experimental standard deviation *(Reproducibility)*

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

- ✓ Type A standard uncertainty: Spread of the distribution of the means:

  Experimental standard deviation of the mean *(Repeatability)*

$$u(x_i) = \frac{s(x_i)}{\sqrt{n}}$$

- ✓ Degrees of freedom

$$\nu_i = n - 1$$

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Example

The potassium concentration in a tap water sample was analysed 5 times (mg/L) by AAS:

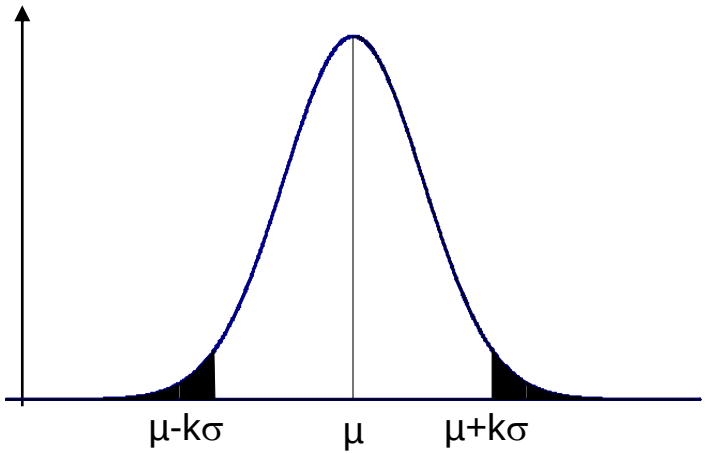
34.62; 36.78; 35.92; 34.17; 35.54

- ✓ Type of Uncertainty: A
- ✓ Probability Distribution: Normal
- ✓ Best estimate of Value: C_P = 35.406 mg/L
- ✓ Standard Uncertainty: s = 1.039 mg/L
  $u(C_P)$ = 0.465 mg/L
- ✓ Degrees of Freedom: 4

Type B evaluation

- Based on other sources of information available:
  - Calibration certificates
  - Manufacturer's specifications
  - Previous measurement data, e.g. control charts
  - Experience of the behaviour of instruments or materials, i.e. scientific/professional judgment
  - Reference data from textbooks

Type B evaluation: Normal



Best estimate	$\mu = \mu$
Standard uncertainty	$u(x_i) = \frac{U}{k}$ $u(x_i) = s(x_i)$
Degrees of freedom	$\nu_i = n-1, or$ $\nu_i = \infty, or$ $\nu_i = Specified$

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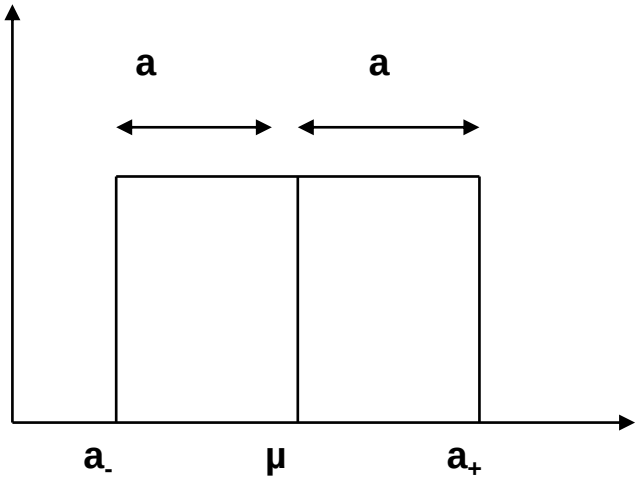
Example

The certificate of analysis for the Cadmium calibration standard has a certified value of 1002.7 ± 1.9 mg/l at a LOC = 90%, ν = 31

- ✓ Type of Uncertainty: B
- ✓ Probability Distribution: Normal
- ✓ Best estimate of Value: C[Cd] = 1002.7 mg/ℓ
- ✓ Standard Uncertainty: U = 1.9 mg/ℓ
  k = 1.70
  u(C[Cd]) = 1.118 mg/ℓ
- ✓ Degrees of Freedom: 31

Type B evaluation: Rectangular



Best estimate	$\mu = \frac{a_+ + a_-}{2}$
Half range	$a = \frac{a_+ - a_-}{2}$
Standard uncertainty	$u(x_i) = \frac{a}{\sqrt{3}}$
Degrees of freedom	$\nu_i = \infty$

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Example

The purity of KHP (Potassium hydrogen phthalate) is quoted in the supplier's catalogue to be within the limit of 99,90% and 100,00%.

- ✓ Type of Uncertainty: B
- ✓ Probability Distribution: Rectangular
- ✓ Best estimate of Value: P = 99.95%
- ✓ Standard Uncertainty: a = 0.05%
  u(P) = 0.0289%
- ✓ Degrees of Freedom: ∞

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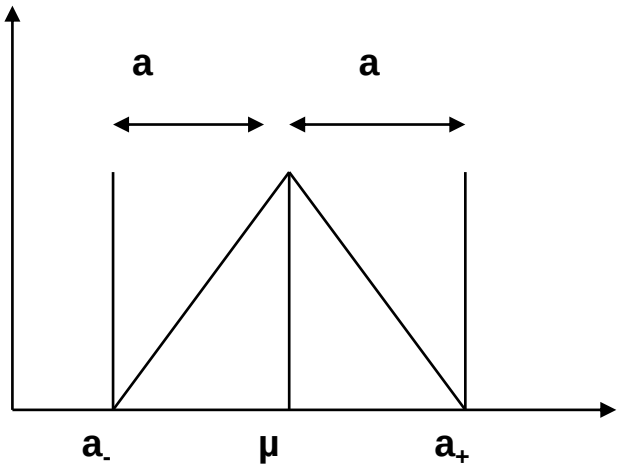
Type B evaluation: Triangular distribution



Best estimate	$\mu = \frac{a_+ + a_-}{2}$
Half range	$a = \frac{a_+ - a_-}{2}$
Standard uncertainty	$u(x_i) = \frac{a}{\sqrt{6}}$
Degrees of freedom	$\nu_i = \infty$

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Example

The manufacturer's specification for the pipette is: 10.0 ± 0.3ml @ 20 °C.

- ✓ Type of Uncertainty: B
- ✓ Probability Distribution: Triangular
- ✓ Best estimate of Value: V = 10.0 mℓ
- ✓ Standard Uncertainty: a = 0.3 mℓ
  u(V) = 0.1732 mℓ
- ✓ Degrees of Freedom: ∞

Step 4: Calculating the combined uncertainty

- All uncertainty components must be in the same unit of measurement
  - Sensitivity coefficients, c_i describes how the output estimate, *y* vary with changes in the input quantities x_1, x_2, … , x_n
  - Calculate sensitivity coefficients, c_i
    - Partial derivatives: $c_i = \frac{\partial f}{\partial x_i}$
    - A numerical estimation: $c_i \approx \frac{\Delta f}{\Delta x_i}$

Step 4: Calculating the combined uncertainty

- ✓ Calculate uncertainty contributions:

$$u(y_i) = c_i \cdot u(x_i)$$

- ✓ Combined standard uncertainty:

$$u_c(y) = \sqrt{\sum (c_i \cdot u(x_i))^2}$$

Step 5: Determine the expanded uncertainty

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

k = coverage factor chosen from the t-distribution table, depending on:

- ✓ the desired level of confidence, and
- ✓ the effective degrees of freedom, ν_{eff} , calculated from the Welch-Satterthwaite formula:

$$\nu_{eff} = \frac{u_c^4(y)}{\sum_{i=1}^{N} \frac{u_i^4(y)}{\nu_i}}$$

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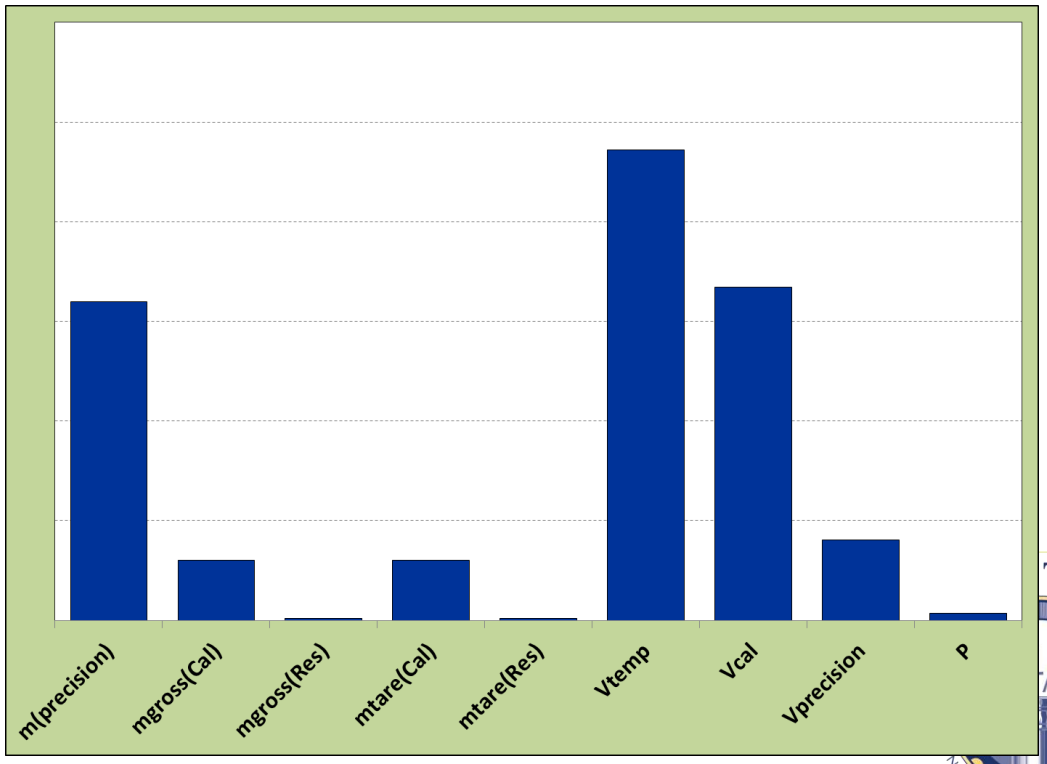
Concluding remarks: GUM approach

- ✓ Provides a framework for assessing uncertainty.
- ✓ Helps to identify and quantify uncertainty sources their contribution to the total uncertainty.



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Method validation
and
Quality Control

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Overview

- ✓ Method Validation
  - ✓ Precision
  - ✓ Trueness (Bias / Recovery)
  - ✓ Linearity
  - ✓ Limit of Detection (LOD) & Limit of Quantification (LOQ)
  - ✓ Selectivity / Specificity
  - ✓ Traceability
- ✓ Quality Control
  - ✓ Mean (x) control chart
  - ✓ Range (R) control chart

Method validation

- ✓ Method validation is required to establish the fitness for purpose of a method for the specific requirements of customers.
- ✓ Method validation studies produce data on:
  - ✓ Overall performance
  - ✓ Individual influence quantities
- ✓ Representative
  - ✓ Sample Matrix
  - ✓ Concentration levels

Validation parameters: Precision

$$s(x_k) = \sqrt{\frac{1}{n-1}\sum_{k=1}^{n}\left(x_k - \bar{x}\right)^2}$$

- ✓ Repeatability standard deviation (s_r)
  - ✓ Short term: 1 lab, 1 day, 1 analyst, 1 instrument, etc.
- ✓ Reproducibility standard deviation (s_R)
  - ✓ Long term: Interlaboratory, months, different analysts, etc.
- ✓ Intermediate precision (s_{zi})
  - ✓ Variation of specific variable(s) only

Validation parameters: Trueness (Bias/Recovery)

- Typically studied through the use of reference materials or spiking studies.
  - Analytical Recovery:

$$\%\,\mathrm{Recovery} = \frac{C_{meas}}{C_{CRM}} \times 100$$

  - Bias:

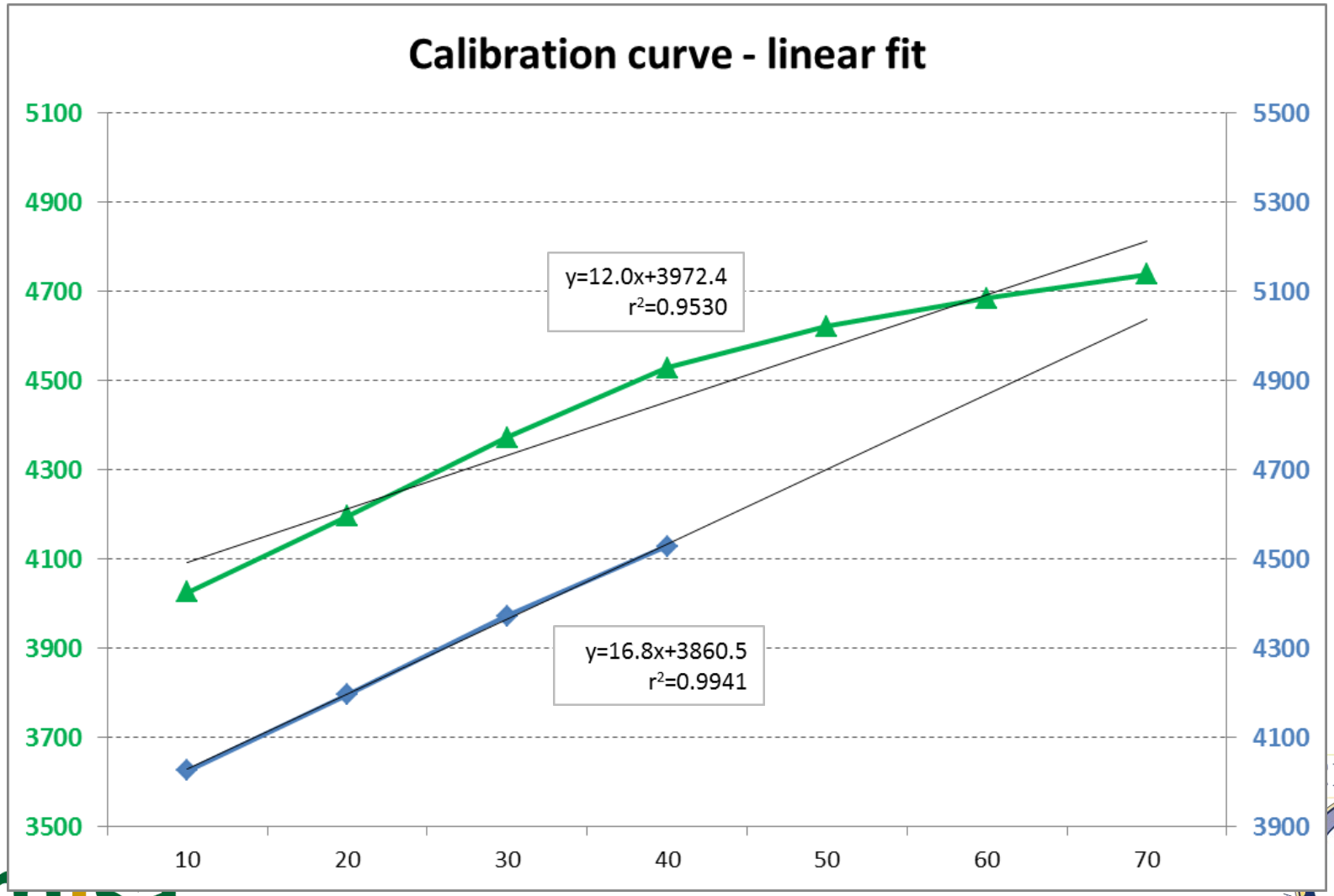
$$\%\,Bias = \frac{C_{meas} - C_{CRM}}{C_{CRM}} \times 100$$

- Expected to be negligible or accounted for.

Validation parameters: Linearity

- ✓ Checked for by:
  - ✓ Inspection
  - ✓ Significance tests for non-linearity (e.g. correlation coefficient, r^2)
- ✓ Non-linearity corrected for by:
  - ✓ Non-linear calibration
  - ✓ Restricted operating range
- ✓ Remaining deviations from linearity accounted for by:
  - ✓ Calibration uncertainty

Validation parameters: Linearity



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  - ✓ Restricted operating range
- ✓ Remaining deviations from linearity accounted for by:
  - ✓ Calibration uncertainty

Validation parameters: Detection limit (LOD)

- ✓ Lowest concentration that can be reliably detected, but not quantified.

$$y_{LOD} = a + 3 \cdot s_{\frac{y}{x}}$$

- ✓ Uncertainties near the detection limit may require careful consideration and special treatment.

Validation parameters: Quantification limit (LOQ)

- ✓ Lowest concentration that can be accurately quantified.

$$y_{LOQ} = a + 10 \cdot s_{y/x}$$

- ✓ Determined to establish the lower end of the practical operating range of a method.
- ✓ Uncertainties near the LOQ may require careful consideration and special treatment.

Validation parameters: Selectivity/specificity

- ✓ The degree to which a method responds uniquely to the required analyte.
- ✓ Investigate the effects of likely interferents by adding the potential interferent to both blank and fortified samples.
- ✓ Can use the data to estimate the uncertainty associated with potential interferences.

Traceability in Analytical Chemistry

- ✓ Traceability – basis for establishing comparability of measurement results
  - ✓ Calibrated equipment
  - ✓ Certified calibration standards
  - ✓ Validated methods
- ✓ Uncertainty is part of the definition
  - ✓ Uncertainty of a traceable result = Uncertainty (reference) + Uncertainty (measurement)

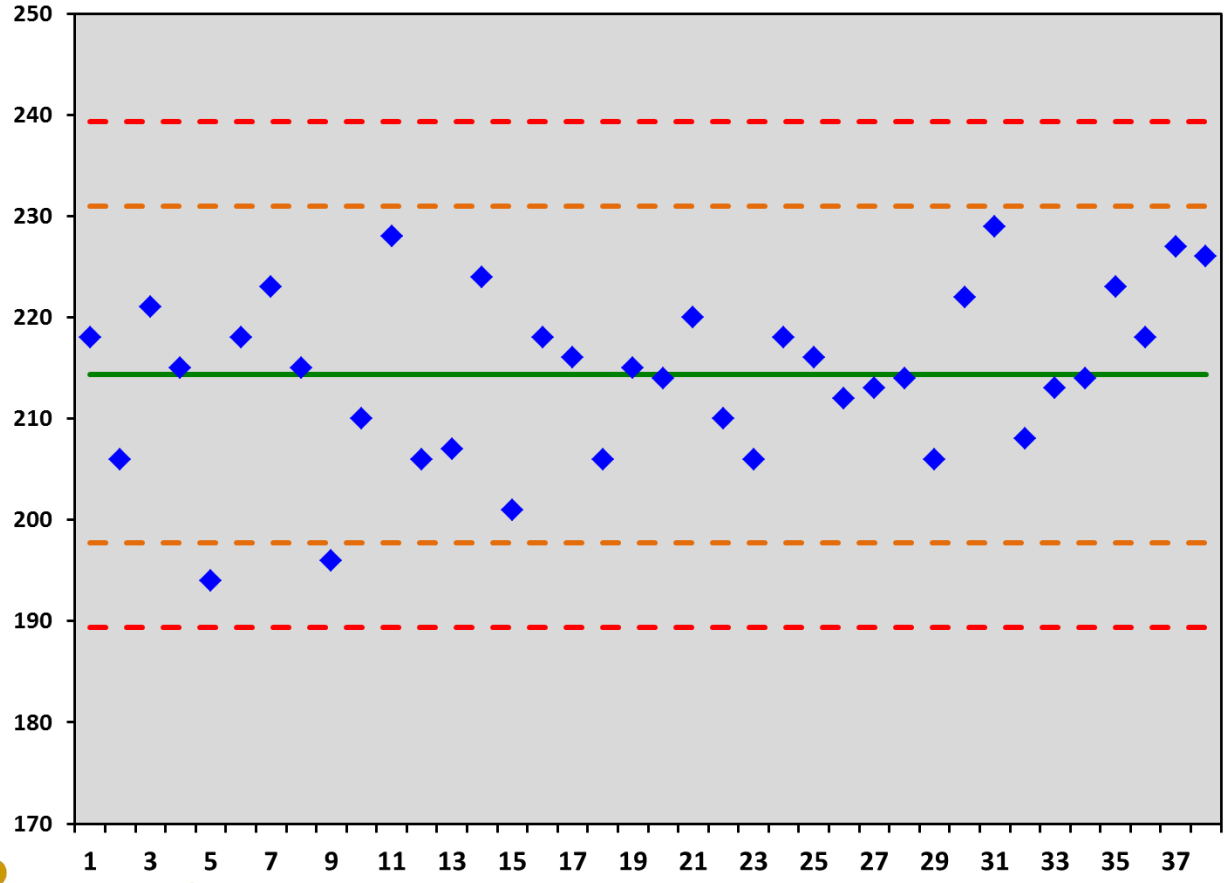
Quality Control: Control Charts

- ✓ Control of the quality of measurements over longer time period.
  - ✓ Trueness
  - ✓ Precision
- ✓ Different control charts
  - ✓ Mean / X-control chart:
    - ✓ Stable homogeneous sample / standard
  - ✓ Range Control chart:
    - ✓ Duplicate samples

Quality Control: Control Sample(s)

- ✓ Requirements:
  - ✓ Representative
    - ✓ Matrix
    - ✓ Concentrations
  - ✓ Sufficient quantities available
  - ✓ Long term stability (if possible)
  - ✓ Homogeneous

Quality Control:
Mean Control Chart



- ✓ Warning limit:
  Mean ± 2SD
- ✓ Action limit:
  Mean ± 3SD

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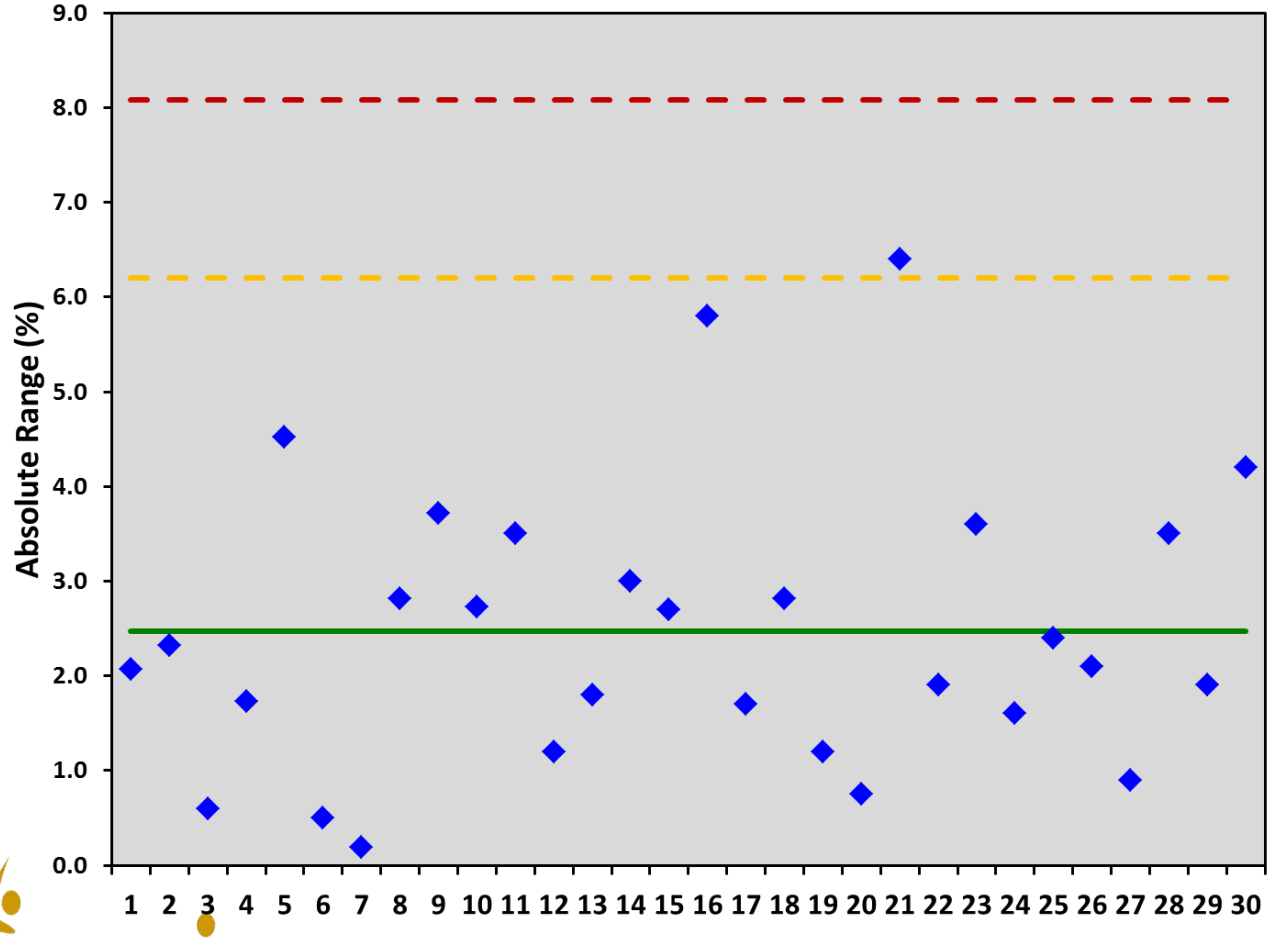
Quality Control: Range Control Chart

- ✓ Real samples analysed in duplicate/triplicate/ etc.
- ✓ Calculate
  - ✓ %Absolute Range
  - ✓ Mean %Range
  - ✓ Standard deviation

$$s = \frac{MeanRange}{d_2}$$

Number of replicate measurements (n)	d_2
2	1.128
3	1.693
4	2.059
5	2.326

Quality Control:
Range Control Chart



- ✓ Warning limit:
  Mean ± 2.83SD
- ✓ Action limit:
  Mean ± 3.69SD

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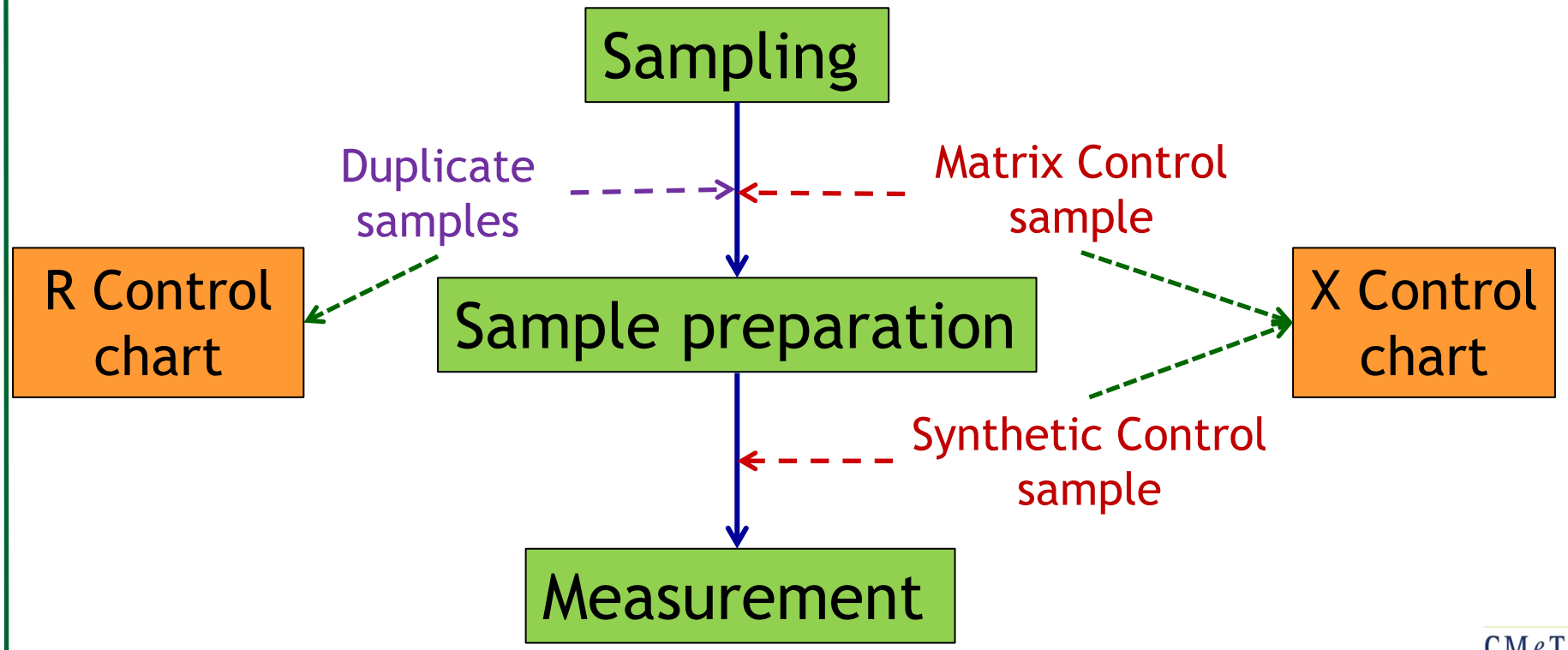
Quality Control: Control Charts

Analytical Process:



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Estimation of Uncertainties in Analytical Measurement

Using Method validation and Quality control data to estimate Measurement Uncertainty

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Challenges in implementation of GUM in Analytical Laboratories

- ✓ Chemical and Microbiological analyses often are very complex testing procedures.
  - ✓ Large number of uncertainty sources that are challenging to quantified separately.
  - ✓ Determining a complete mathematical model to describe method.
  - ✓ Large number of routine tests for various measurands (analytes), concentration levels and in variety of matrices.

Simplification of GUM-approach for Analytical Laboratories

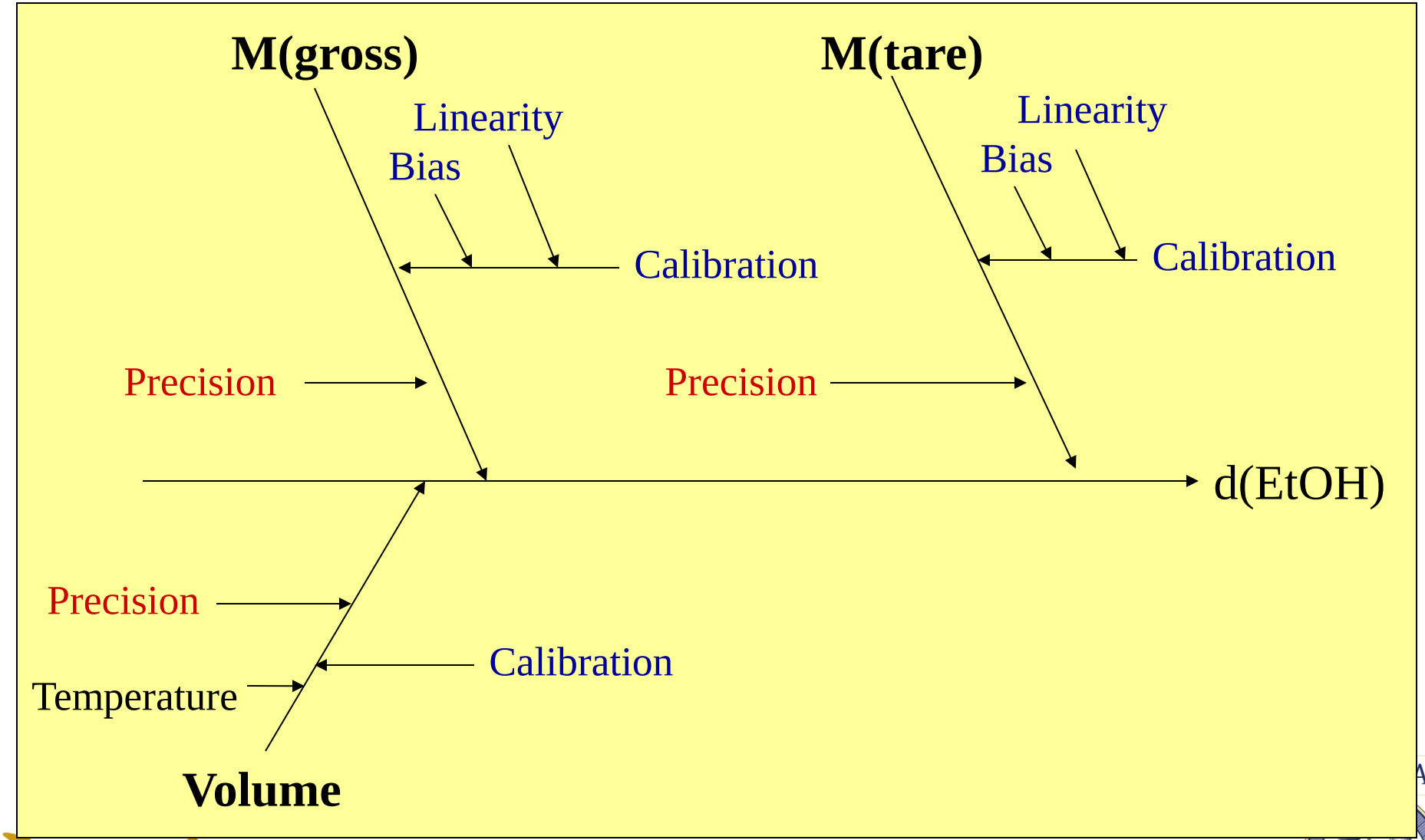
- ✓ Bottom-Up (GUM) vs Top Down approach:
  - ✓ Using method validation and quality control data
- ✓ NORDTEST - Handbook for calculation of measurement uncertainty in environmental laboratories
  - ✓ Goal: Provide a practical, understandable and common way of measurement uncertainty calculations, based on existing quality control and validation data.
  - ✓ Report TR 537: www.nordicinnovation.net/nordtest.cfm

NORDTEST-Approach

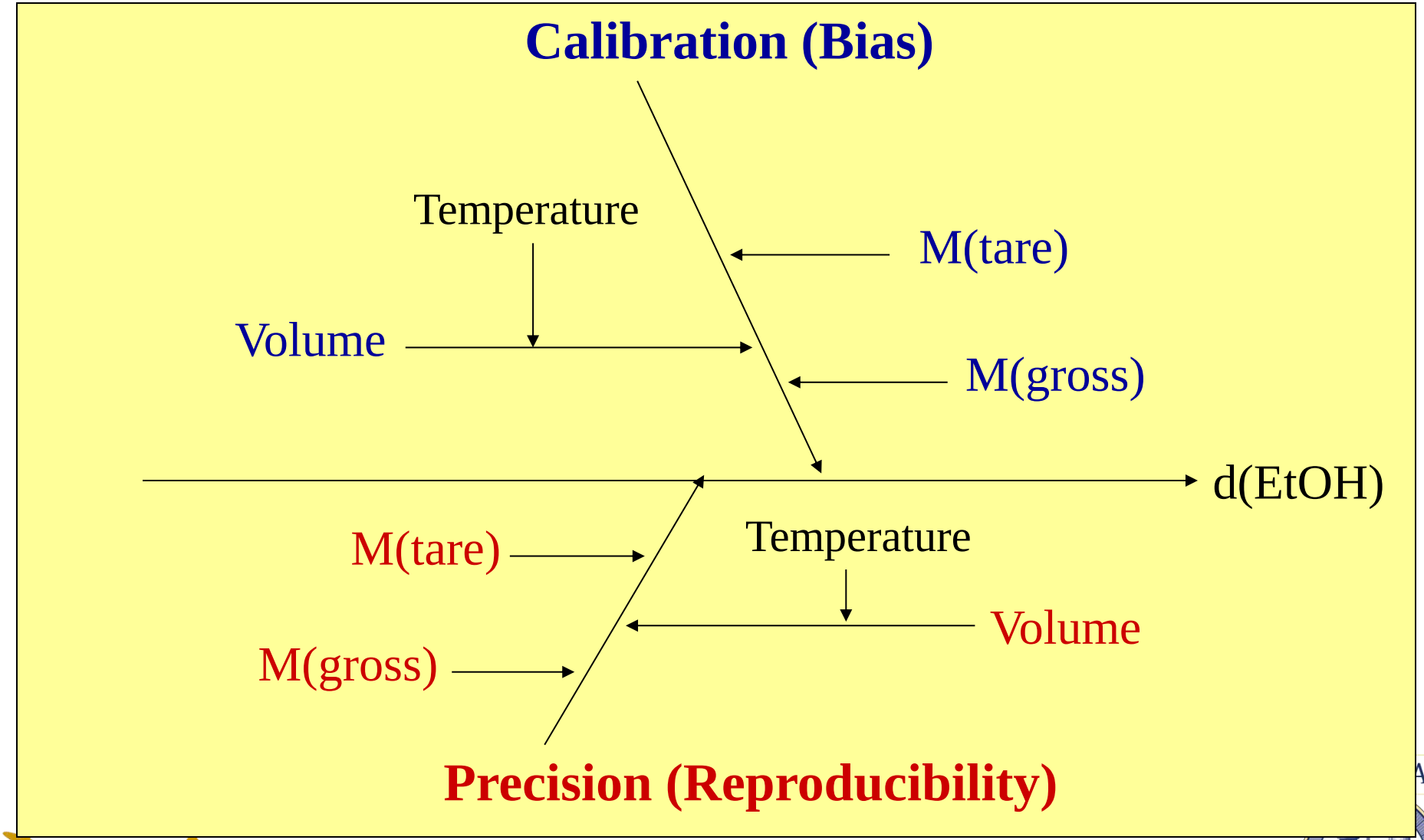
- ✓ Combination of:
  - ✓ Reproducibility within the laboratory
  - ✓ Estimation of the method and laboratory bias

- ✓ Provided that reproducibility and bias data is representative:
  - ✓ Different stock standard solutions
  - ✓ Different batches of reagents
  - ✓ Re-calibration of instruments
  - ✓ Representative period of time – ideally 1 year
  - ✓ Minimum number of results: 50

Cause and Effect diagram: GUM



Cause and Effect diagram: NORDTEST



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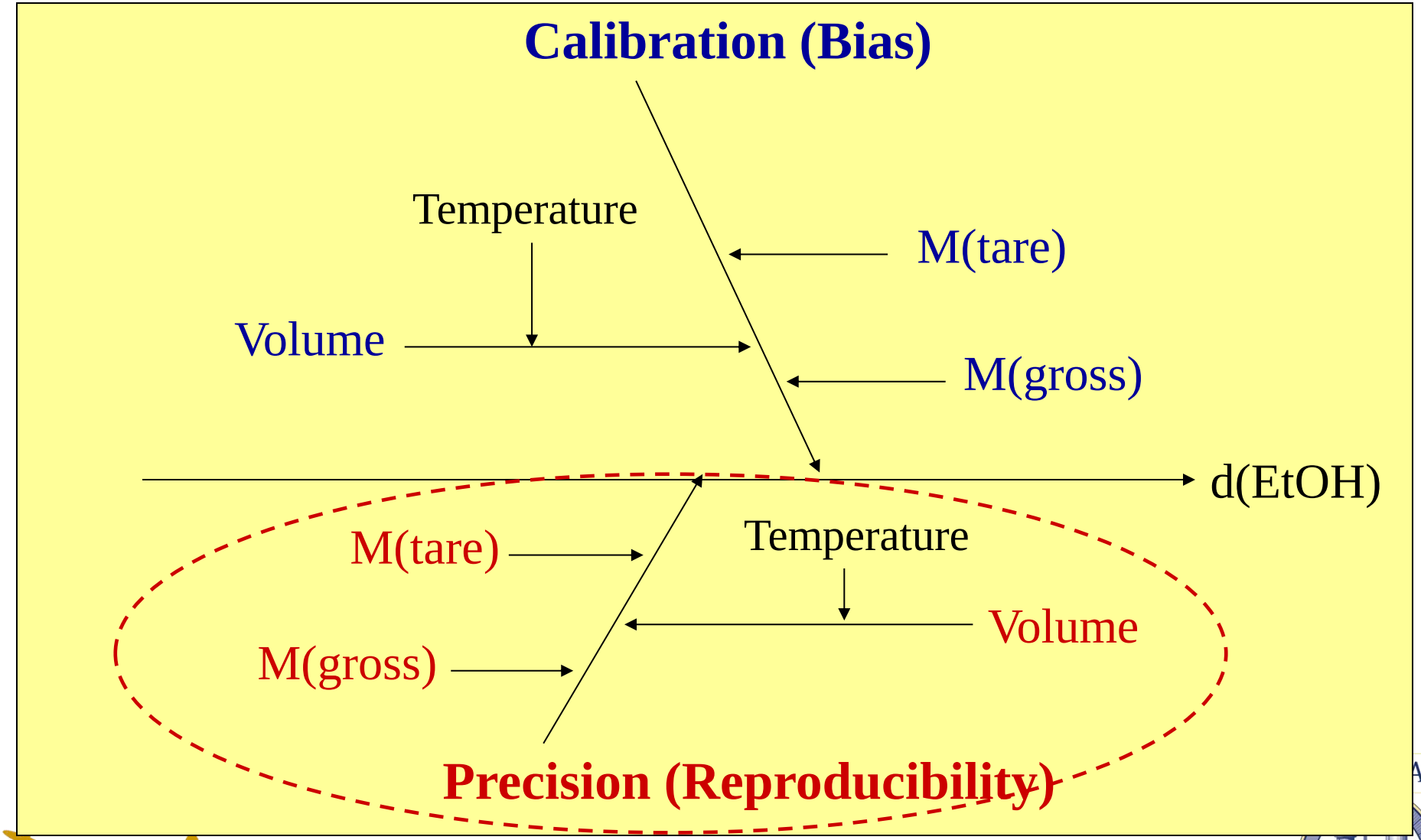
NORDTEST Step 3

- ✓ Quantify uncertainty components
  - ✓ 3.1: Within laboratory reproducibility
  - ✓ 3.2: Method and laboratory bias
  - ✓ 3.3: Additional factors

$$\%u = \frac{u(x_i)}{x_i} \times 100$$

3.1: Within-Laboratory Reproducibility



NORDTEST Step 3.1

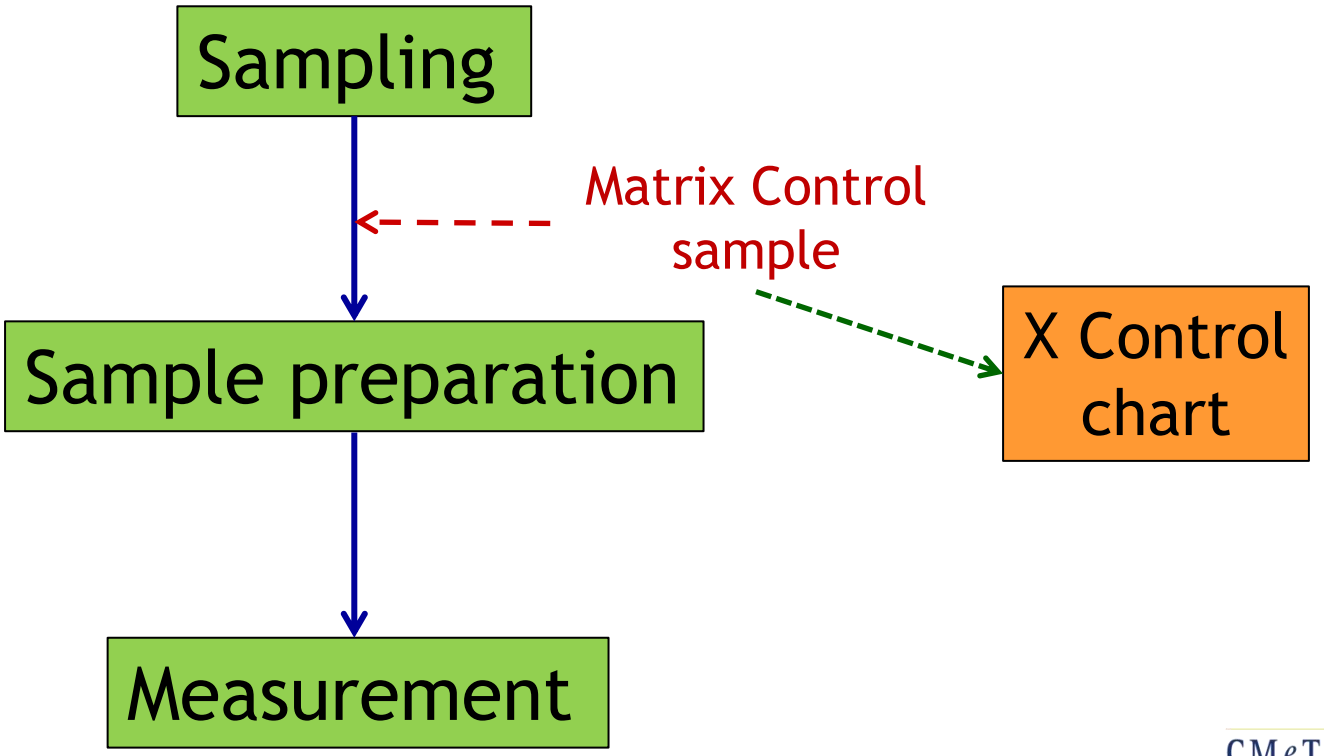
- ✓ Within laboratory reproducibility, R_w
  - ✓ Control sample covering the whole analytical process
  - ✓ Control sample not covering the whole process, matrix different
  - ✓ Unstable samples – no control sample

3.1: Reproducibility within the laboratory: R_w

Control sample covering the whole analytical process

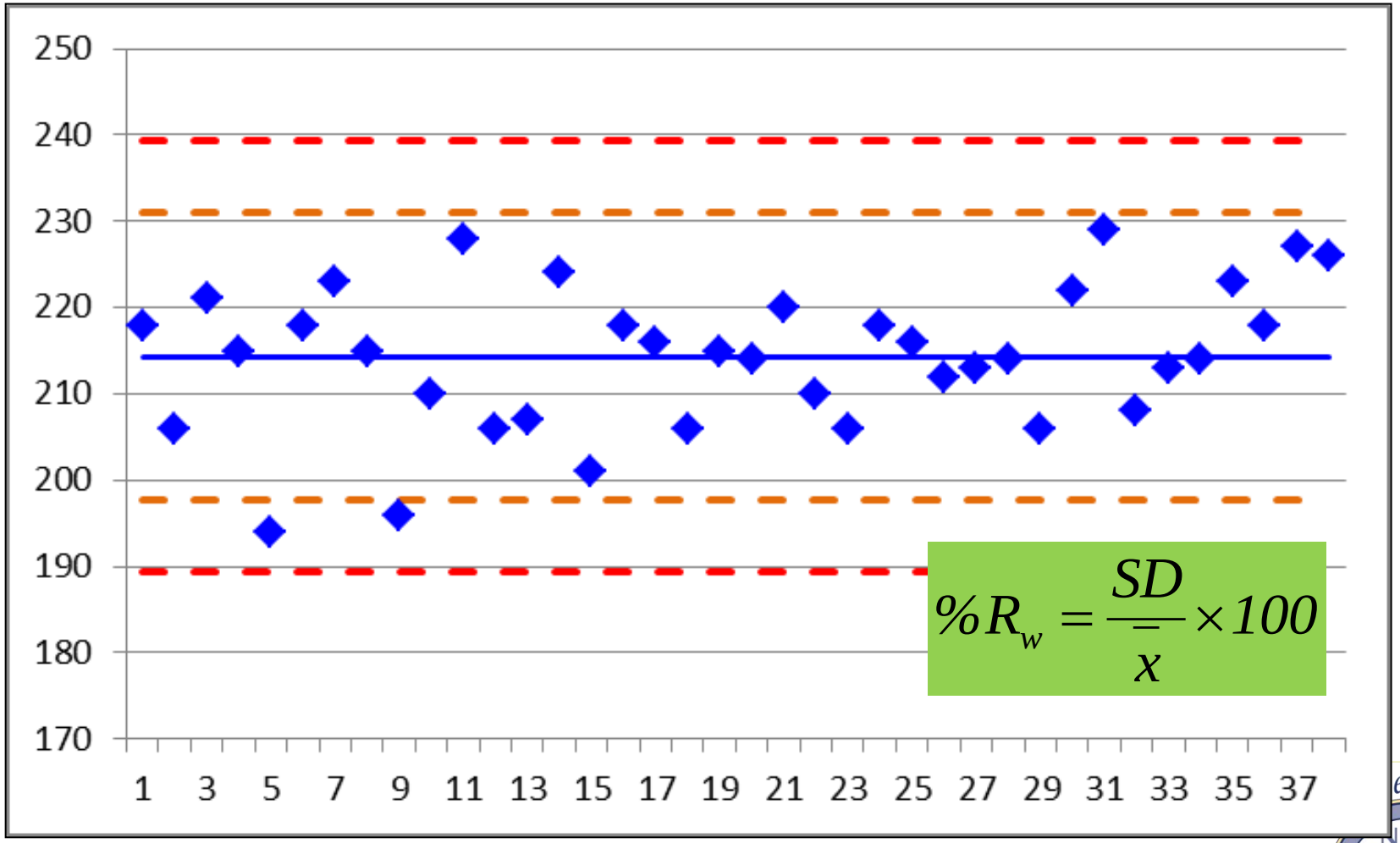
- If
  - Control sample covers the whole analytical process, and
  - Control samples have a matrix similar to the samples, then:
- The within-laboratory reproducibility at that concentration level can be estimated from the analyses of the control sample.
- If the analyses performed cover a wide range of concentration levels, control samples of other concentration levels should also be used.

Analytical Process:



3.1: Reproducibility within the laboratory: R_w

Mean Control Chart



3.1: Reproducibility within the laboratory: R_w

Control sample covering the whole analytical process

✓ Example:

Reproducibility within the lab R_w

Mean Control chart		% Relative Uncertainty (% R_w)	Comments
Mean	**s_{Rw} - value**		
Control sample 1: $\bar{X}$ = 20.01 µg/l	Standard deviation: s_{Rw} = 0.5 µg/l	**2.5%**	from 75 measurements in 2002
Control sample 2: $\bar{X}$ = 250.3 µg/l	Standard deviation: s_{Rw} = 3.7 µg/l	**1.5%**	from 50 measurements in 2002

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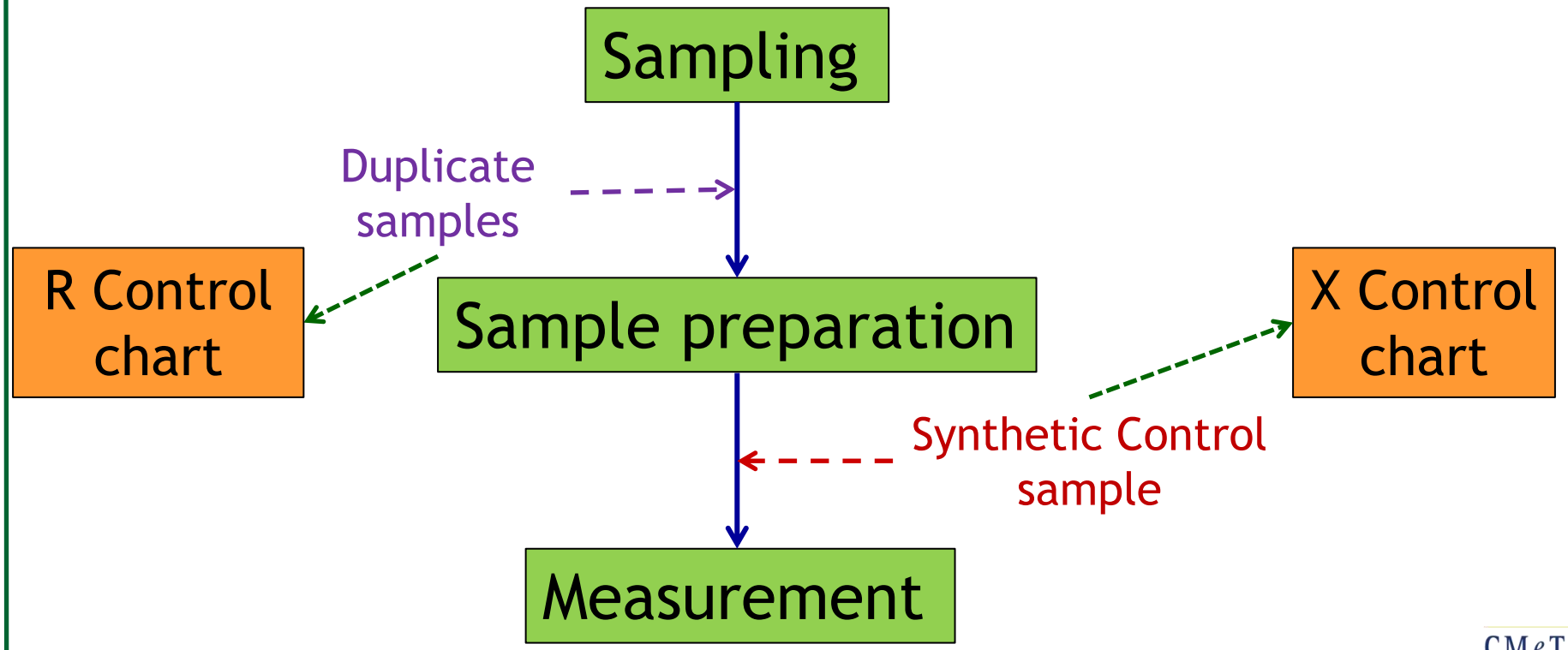
3.1: Reproducibility within the laboratory: R_w

Control sample not covering the whole process, matrix different

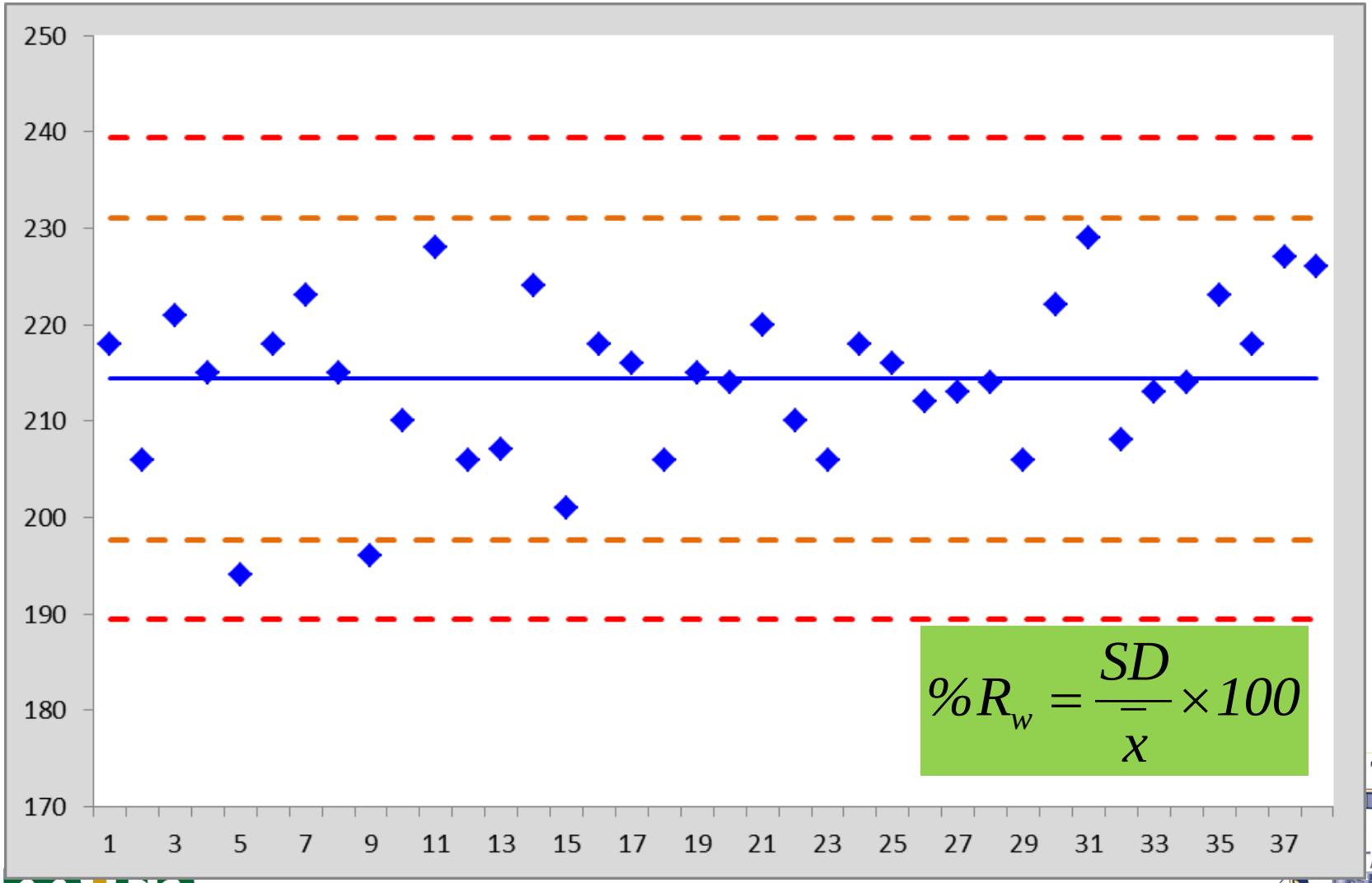
- If:
  - A synthetic control solution is used for quality control, and
  - The matrix type of the control sample is **not** similar to the natural samples, then:
- Mean Control Chart: Long term reproducibility contribution, but not does not include uncertainties arising from different matrices and sample preparation procedures.
- Range control chart: Estimate the repeatability from different matrices and sample preparation processes.

Analytical Process:



3.1: Reproducibility within the laboratory: R_w

Mean Control Chart



$$\%R_w = \frac{SD}{\bar{x}} \times 100$$

3.1: Reproducibility within the laboratory: R_w

Range control data: Duplicate analyses (n=2)

Sample No	Result 1	Result 2	Mean	Range	ABS (%Range)
1	37.62	36.85	37.235	0.77	2.068
2	16.18	16.56	16.37	-0.38	2.321
3	28.82	28.65	28.735	0.17	0.592
4	4490	4413	4451.5	77	1.730
5	135.7	129.7	132.7	6.0	4.521
6	62.56	62.25	62.405	0.31	0.497
7	158.9	159.2	159.05	-0.3	0.189
8	16540	16080	16310	460	2.820
9	31.26	30.12	30.69	1.14	3.715
10	58.49	60.11	59.3	-1.62	2.732
				%Mean (ABS)	2.119

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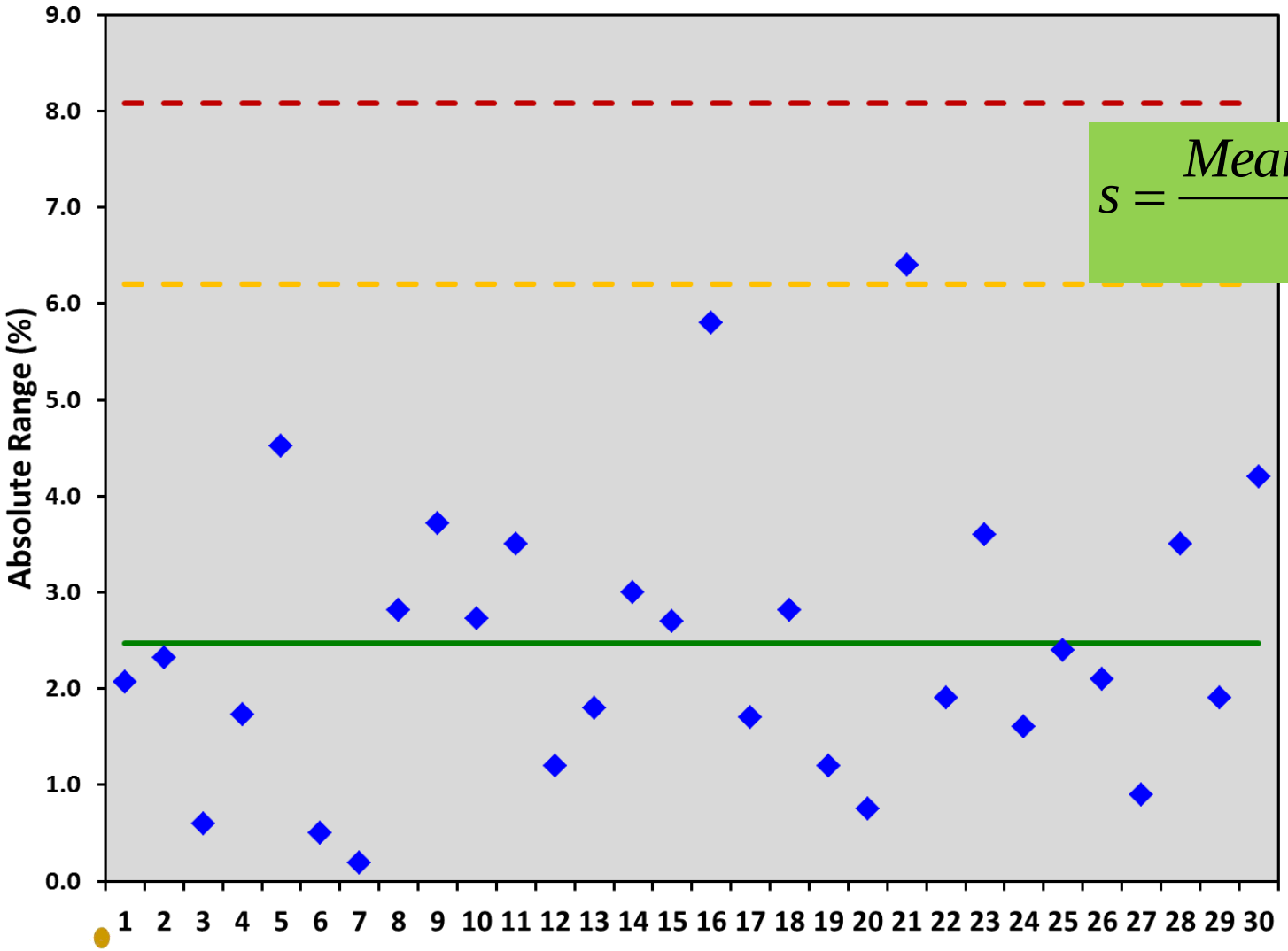
3.1: Reproducibility within the laboratory: R_w

Range control chart



$$s = \frac{MeanRange}{d_2}$$

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3.1: Reproducibility within the laboratory: R_w

Control sample not covering the whole process, matrix different

✓ Example:

Reproducibility within the lab R_w

	s_{Rw} - value	Calculation	%Uncertainty (%R_w)
Low level: 2-15 µg/l	Mean control chart: $s_{Rw} = 1.5\%$ Range control chart: $s_{rw} = 5.18 / 1.128 = 4.6\%$	$u(x) = \sqrt{1.5\%^2 + 4.6\%^2}$	4.8%
High level: >15 µg/l	Mean control chart: $s_{Rw} = 1.5\%$ Range control chart: $s_{rw} = 4.06 / 1.128 = 3.6\%$	$u(x) = \sqrt{1.5\%^2 + 3.6\%^2}$	3.9%

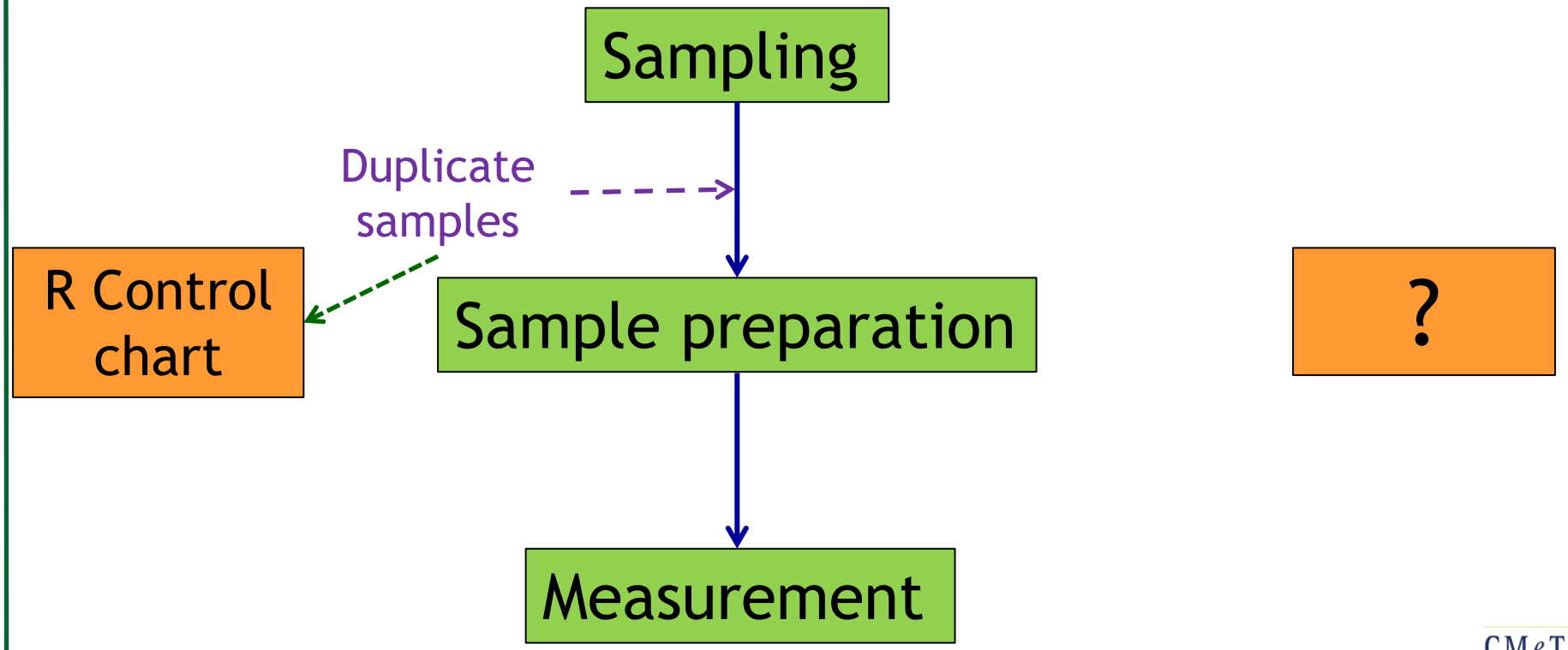
Note: The repeatability component is included twice

3.1: Reproducibility within the laboratory: R_w

Unstable control samples

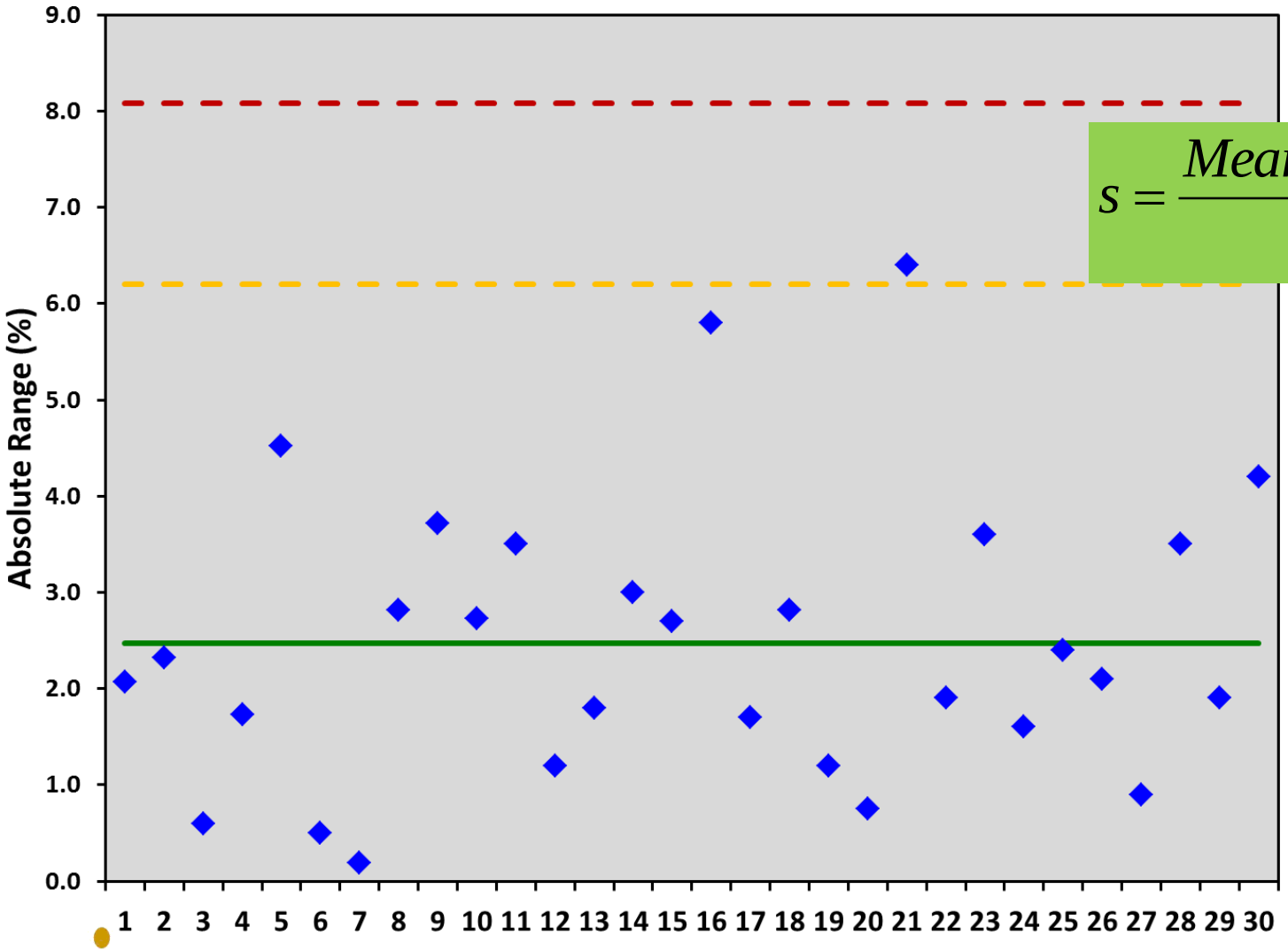
- If
  - The laboratory does not have access to stable control samples, then:
- It is only possible to estimate uncertainty components from repeatability via the range control chart.
- The „long-term“ uncertainty component (from batch to batch) has to be estimated e.g. by expert judgement.

Analytical Process:



3.1: Reproducibility within the laboratory: R_w

Range control chart



$$s = \frac{MeanRange}{d_2}$$

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3.1: Reproducibility within the laboratory: R_w

Unstable control samples

✓ Example:

Reproducibility within the lab R_w

	s - value	Relative Uncertainty (R_w)
Range Control of natural samples (n=2)	s = 0.024 mg/l mean: 7.53 mg/l	0.32%
Estimated variation from differences in calibration over time	s = 0.5 %	0.5%
Combined uncertainty for R_w	Repeatability + Reproducibility in calibration $\sqrt{0.32\%^2 + 0.5\%^2} = 0.59\%$	

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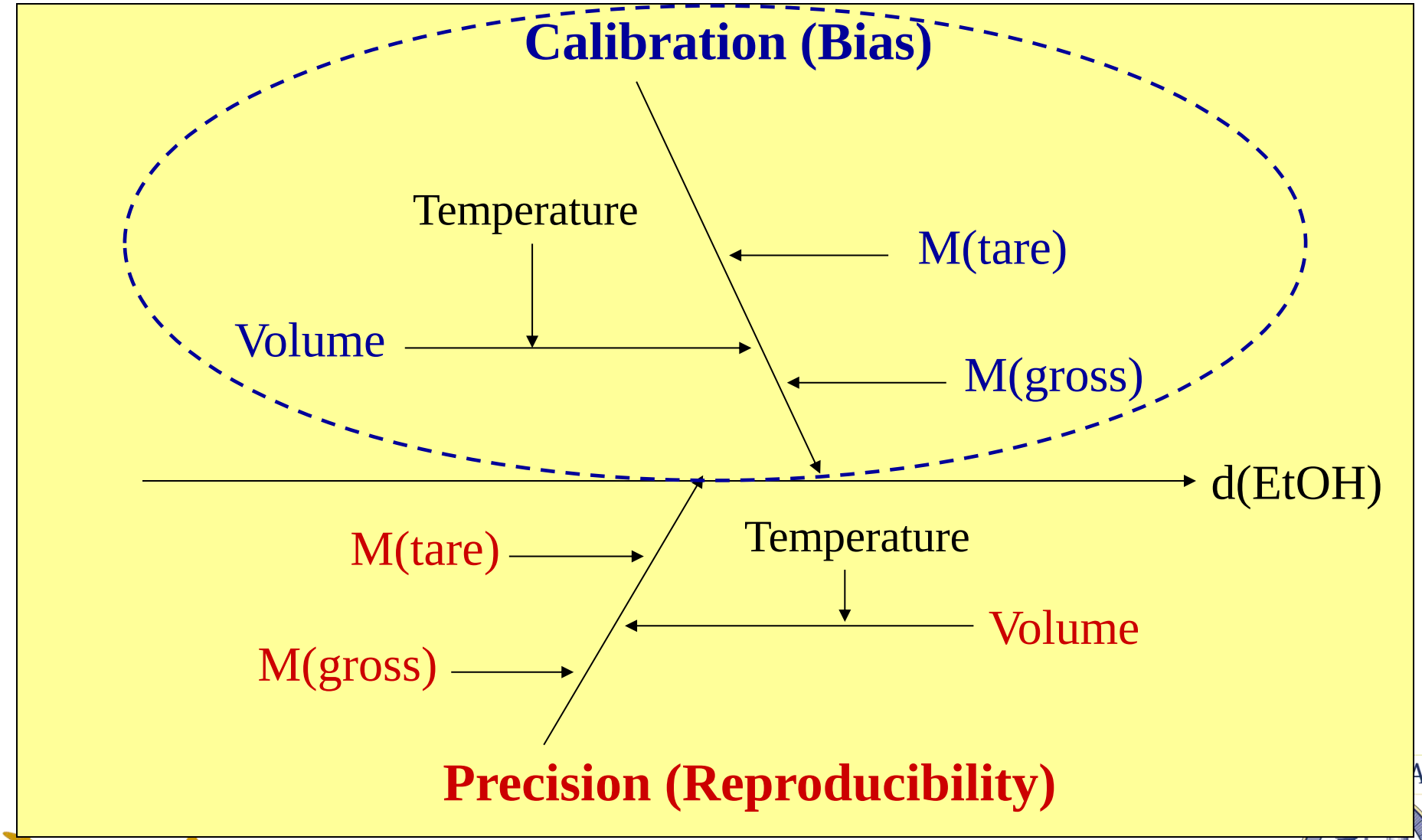
3.2: Laboratory and Method Bias



NORDTEST Step 3.2

- Method and Laboratory bias:
  - Sources of bias should always be eliminated if possible.
  - According to GUM a measurement result should always be corrected if the bias is significant, constant and based on reliable data, such as a CRM.
  - In many cases the bias can vary depending on changes in matrix. This can be identified when analysing several matrix CRMs.

Method and Laboratory Bias: $\%u_{Bias}$

- ✓ Consists of 2 components:
  - ✓ %Bias: %Difference from the reference value
  - ✓ Uncertainty of the reference value: $\%u(C_{ref})$
- ✓ Method and laboratory bias, $\%u_{Bias}$, can be estimated from:
  - ✓ Use of several Certified Reference Materials
  - ✓ Use of one Certified Reference Material
  - ✓ Use of Proficiency Testing / Interlaboratory Comparison data
  - ✓ Use of Recovery Data

3.2: Method and Laboratory bias: u_{bias}

Use of several certified reference material

- When several CRMs are analysed:
  - Bias:

$$RMS_{bias} = \sqrt{\frac{\sum (bias_i)^2}{n}}$$

  - Uncertainty of the Reference Values:
    - Employ GUM-approach for individual uncertainties
    - Combine:

$$u(C_{ref}) = \frac{\sum u\left(C_{ref(i)}\right)}{n}$$

- Uncertainty of the Bias:

$$u_{bias} = \sqrt{RMS_{bias}^2 + u(C_{ref})^2}$$

3.2: Method and Laboratory bias: u_{bias}

Use of several certified reference material

- ✓ Example:

	% Bias	% Standard deviation	n	$\%u(C_{ref})$
CRM 1	3.48%	2.2%	12	2.21%
CRM 2	-0.9%	2.0%	7	1.8%
CRM 3	2.4%	2.8%	10	1.8%

3.2: Method and Laboratory bias: u_{bias}

Use of several certified reference material

- ✓ Quantification of the %Bias:

$$RMS_{bias} = \sqrt{\frac{\sum (bias_i)^2}{n}} = \sqrt{\frac{3.48\%^2 + (-0.9\%)^2 + 2.4\%^2}{3}} = 2.5\%$$

- ✓ Uncertainty of the certified value $u(C_{ref})$:

$$u(C_{ref}) = \frac{\sum u\left(C_{ref\,(i)}\right)}{n} = \frac{2.21 + 1.8 + 1.8}{3} = 1.9\%$$

- ✓ Then the Uncertainty of the Bias is:

$$u_{bias} = \sqrt{RMS_{bias}^2 + u(C_{ref})^2} = \sqrt{2.5\%^2 + 1.9\%^2} = 3.1\%$$

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3.2: Method and Laboratory bias: u_{bias}

Use of one certified reference material

- ✓ If only one CRM is analysed:

$$u_{bias} = \sqrt{(bias)^2 + \left(\frac{s_{bias}}{\sqrt{n}}\right)^2 + u(C_{ref})^2}$$

- ✓ The reference material should be analysed in at least 5 different analytical series.

3.2: Method and Laboratory bias: u_{bias}

Use of one certified reference material

- Example:
  - A CRM was analysed 12 times. The mean is 11.9 mg/L with a standard deviation of 2.2%.
  - Certified value: 11.5 ± 0.5 mg/L (95% confidence interval)

- Quantify the %Bias:

$$\%Bias = 100 \cdot (11.9 - 11.5) / 11.5 = 3.48\% \quad and$$

$$\%s_{bias} = 2.2\% \quad with \quad n = 12$$

3.2: Method and Laboratory bias: u_{bias}

Use of one certified reference material

- ✓ Example (cont):
- ✓ Quantify the uncertainty of the reference material:

Uncertainty component from the uncertainty of the certified value **Certified value: 11.5 ± 0.5 mg/L (95% confidence interval)**	
Convert the confidence Interval:	Expanded Uncertainty (Type B, Normal distribution): U = 0.5 mg/L k = 1.96 Standard uncertainty: 0.5/1.96 = 0.26 mg/L
Convert to %Relative uncertainty: $\%u(C_{ref})$	(0.26/11.5)x100 = 2.21%

3.2: Method and Laboratory bias: u_{bias}

Use of one certified reference material

- ✓ Therefore the Bias uncertainty is:

$$u_{bias} = \sqrt{(bias)^2 + \left(\frac{s_{bias}}{\sqrt{n}}\right)^2 + u(C_{ref})^2}$$

$$= \sqrt{(3.48\%)^2 + \left(\frac{2.2\%}{\sqrt{12}}\right)^2 + 2.21\%^2} = 4.2\%$$

3.2 Method and Laboratory bias: u_{bias}

Use of Proficiency Testing (PT) results

- Laboratory should participate at least 6 times within a reasonable time interval.
  - Bias: $$RMS_{bias} = \sqrt{\frac{\sum (bias_i)^2}{n}}$$
  - Uncertainty of PT Reference Value:
    - Individual PT results:

Arithmetic means	Robust means
$u(C_{ref})_i = \frac{s_{R,i}}{\sqrt{n_{T,i}}}$	$u(C_{ref})_i = 1{,}25 \cdot \frac{s_{R,i}}{\sqrt{n_{T,i}}}$

    - Combined Uncertainty of Reference value:

$$u(C_{ref}) = \frac{\sum_i u(C_{ref})_i}{n_R}$$

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3.2 Method and Laboratory bias: u_{bias}

Use of Proficiency Testing (PT) results

✓ Example:

Uncertainty of the reference value $u(C_{ref})$

Data from the PT/ILC:

- For robust means:

$$u(C_{ref})_i = 1{,}25 \cdot \frac{s_{R,i}}{\sqrt{n_{T,i}}}$$

$s_{R,1}$ = 3,1%, $n_{T,1}$ = 28	$u(C_{ref})_1$ = 0,73%
$s_{R,2}$ = 4,8%, $n_{T,2}$ = 28	$u(C_{ref})_2$ = 1,13%
$s_{R,3}$ = 7,6%, $n_{T,3}$ = 28	$u(C_{ref})_3$ = 1,80%
$s_{R,4}$ = 5,3%, $n_{T,4}$ = 35	$u(C_{ref})_4$ = 1,12%
$s_{R,5}$ = 6,9%, $n_{T,5}$ = 35	$u(C_{ref})_5$ = 1,46%
$s_{R,6}$ = 8,4%, $n_{T,6}$ = 35	$u(C_{ref})_6$ = 1,77%

$$u(C_{ref}) = \frac{\sum_i u(C_{ref})_i}{n_R}$$

$u(C_{ref})$ = 1,34%

3.2 Method and Laboratory bias: u_{bias}

Use of Proficiency Testing (PT) results

- ✓ Quantification of the %Bias:
  - ✓ In the 6 participations the biases have been: 2%, 7%, -2%, 3%, 6% and 5%

$$RMS_{bias} = \sqrt{\frac{\sum (bias_i)^2}{n}}$$

$$= \sqrt{\frac{2\%^2 + 7\%^2 + (-2\%)^2 + 3\%^2 + 6\%^2 + 5\%^2}{6}} = 4.6\%$$

3.2 Method and Laboratory bias: u_{bias}

Use of Proficiency Testing (PT) results

- ✓ Then the Uncertainty of the Bias is:

$$u_{bias} = \sqrt{RMS_{bias}^2 + u(C_{ref})^2}$$

$$= \sqrt{4.6\%^2 + 1.34\%^2} = 4.8\%$$

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3.2: Method and Laboratory bias: u_{bias}
From Recovery Tests

- Recovery tests can be used to estimate bias:
  - Bias: $$RMS_{bias} = \sqrt{\frac{\sum (bias_i)^2}{n}}$$
  - Uncertainty of Reference Value:
    - Use GUM-approach to quantify
  - Uncertainty of Bias

$$u_{bias} = \sqrt{RMS_{bias}^2 + u(C_{ref})^2}$$

3.2: Method and Laboratory bias: u_{bias}
From Recovery Tests

✓ Example:

In an experiment the recoveries for an added spike were 95 %, 98 %, 97 %, 96 %, 99 % and 96 % for 6 different sample matrices. The spike of 0.5 ml was added with a micropipette.

Uncertainty of reference value	
uncertainty of the concentration of the spike u(conc)	from the certificate: 95% confidence interval = ± 1.2 % $u(conc) = 0.6\%$
uncertainty of the added volume u(vol)	from the manufacturer of the micro pipette: max. bias: 1% (rectangular interval), repeatability: max. 0.5% (standard dev.) $u(vol) = \sqrt{\left(\frac{1\%}{\sqrt{3}}\right)^2 + 0.5\%^2} = 0.76\%$
uncertainty of the reference value $u(c_{recovery})$	$\sqrt{u(conc)^2 + u(vol)^2} = \sqrt{0.6\%^2 + 0.76\%^2} = 1.0\%$

3.2: Method and Laboratory bias: u_{bias} From Recovery Tests

- Example (cont):
  - Quantification of the bias:

$$RMS_{bias} = \sqrt{\frac{5\%^2 + 2\%^2 + 3\%^2 + 4\%^2 + 1\%^2 + 4\%^2}{6}} = 3.44\%$$

- Then the Uncertainty of the Bias is:

$$u_{bias} = \sqrt{RMS_{bias}^2 + u(C_{recovery})^2} = \sqrt{3.44\%^2 + 1.0\%^2} = 3.6\%$$

3.3 Additional factors: $u(f_i)$

- ✓ Uncertainty contributions not incorporated into precision and bias data.
  - ✓ GUM-approach:
    - ✓ Type A
    - ✓ Type B
  - ✓ Experimentally:
    - ✓ Study of the effect of a variation of a single parameter on the result.
    - ✓ Robustness studies, systematically examining the significance of moderate changes in parameters.
    - ✓ Systematic multifactor experimental designs.

NORDTEST: Step 4

- ✓ Calculate Combined Standard Uncertainty (u_c)
  - ✓ Reproducibility (R_w): From control samples and other estimations
  - ✓ Bias (u_{bias}): From CRM, PT or recovery tests
  - ✓ Additional factors (f_i)

$$\%u_c = \sqrt{\%u(R_w)^2 + (\%u_{bias})^2 + \%u(f_i)^2}$$

All expressed as % relative uncertainty

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NORDTEST: Step 5

- Determine the expanded uncertainty:

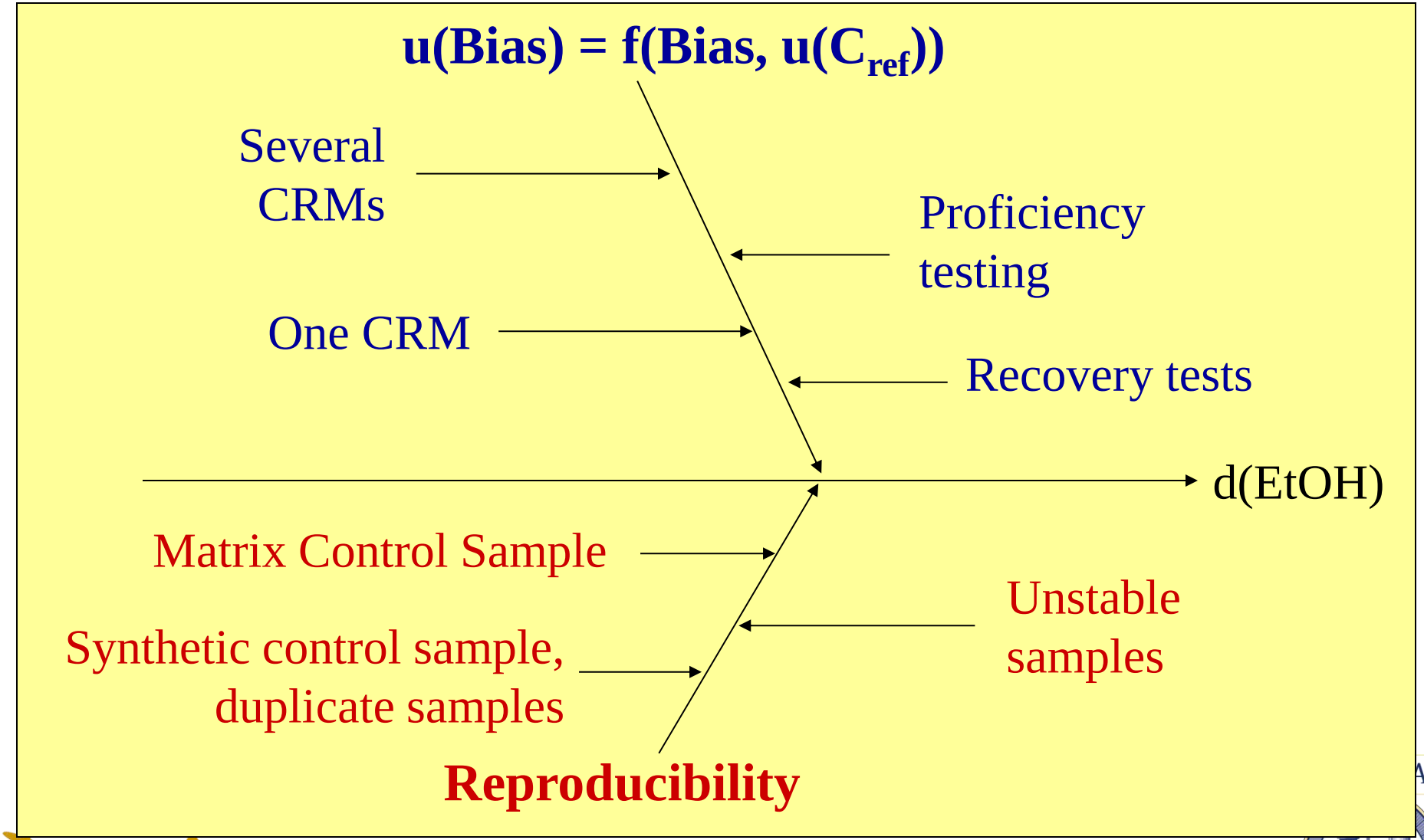
$$U = k \times u_c(y)$$

  - The NORDTEST-approach adopts k=2 for an approximate level of confidence of 95% with assumed effective degrees of freedom > 30.

NORDTEST: Step 6

- ✓ Reporting final result (with measurement unit):
  - ✓ Result (Y)
  - ✓ Expanded Uncertainty (U)
  - ✓ Coverage factor (k)
  - ✓ Level of confidence (LOC)
  - ✓ Estimation method used, e.g.
    - ✓ Measurement uncertainty derived from interlaboratory comparison data

Nordtest – approach: Summary



Conclusions

- ✓ Bottom Up (GUM)
  - ✓ Mathematical model needed
  - ✓ Complex calculations
  - ✓ Smaller uncertainties
- ✓ Top Down (Nordtest, Eurachem/CITAC)
  - ✓ No model needed
  - ✓ Simpler combination of data already available in accredited laboratory
  - ✓ Uncertainties are larger, but perhaps more realistic?
- ✓ Fit for purpose?

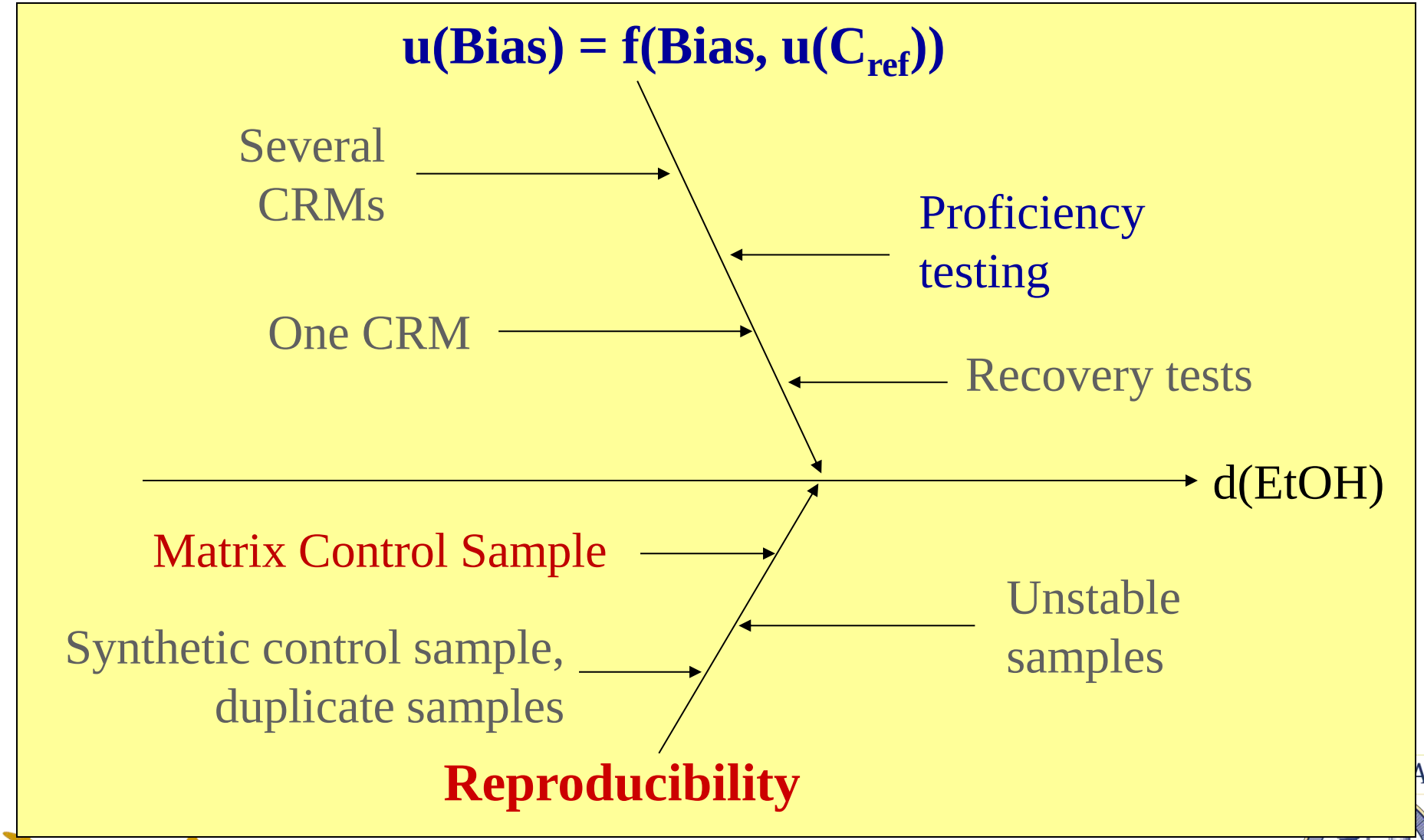
Example

SADCWater PT: Trace Elements (Ni) in drinking water

The laboratory routinely analyses an in-house drinking water quality control solution.

The laboratory doesn't have a CRM, but participates in a PT scheme on trace elements in drinking water.

Nordtest-approach: Ni in drinking water



Analysis of Nickel in drinking water

Reproducibility

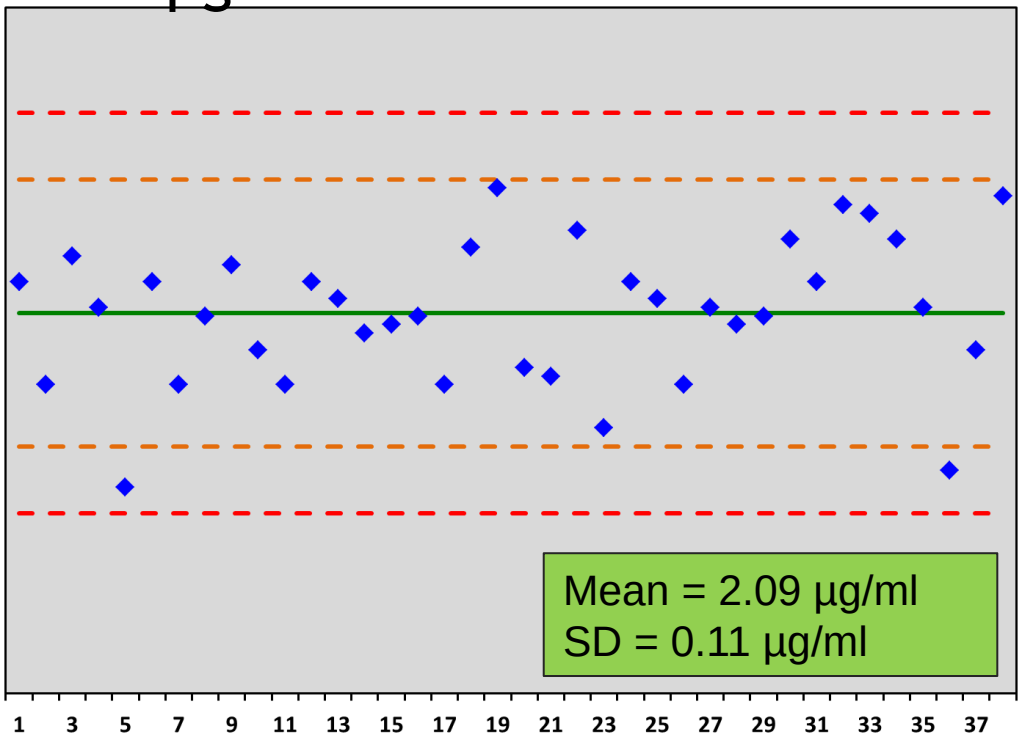
The laboratory routinely analyse an in-house drinking water solution:

- ✓ Concentration = 2.0 µg/ml Ni.
- ✓ From 40 measurements of the solution:
  - ✓ Mean = 2.09 µg/ml
  - ✓ Standard deviation = 0.11 µg/ml

$$\%s_{R_w} = \frac{SD}{\bar{x}} \times 100$$

$$= \frac{0.11}{2.09} \times 100$$

$$= 5.26\%$$



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Analysis of Nickel in drinking water

Bias

The laboratory doesn't have a CRM, but participates in a PT scheme on nickel in drinking water. The coordinating laboratory prepares the sample gravimetrically and uses this value as the assigned value. The following results were obtained over the past 3 rounds.

Analysis of Nickel in drinking water

Bias

PT no.	Assigned value	Standard Uncertainty	$\%u(C_{ref})$	Laboratory Result	%Bias
PT10-S4	0.53172	0.00271	0.51	0.5304	-0.25
PT10-S5	0.08815	0.00027	0.31	0.0853	-3.23
PT10-S6	0.92701	0.00273	0.29	0.9409	1.50
PT11-S4	0.63197	0.00272	0.43	0.6140	-2.84
PT11-S5	0.05642	0.00027	0.48	0.0574	1.74
PT11-S6	0.92854	0.00274	0.30	0.9490	2.20
PT12-S4	0.84745	0.00178	0.21	0.9130	7.73
PT12-S5	1.17067	0.00182	0.16	1.150	-1.77
PT12-S6	0.57679	0.00176	0.31	0.5910	2.46

Analysis of Nickel in drinking water

Bias

PT no.	%u(C_{ref})	%Bias
PT10-S4	0.51	-0.25
PT10-S5	0.31	-3.23
PT10-S6	0.29	1.50
PT11-S4	0.43	-2.84
PT11-S5	0.48	1.74
PT11-S6	0.30	2.20
PT12-S4	0.21	7.73
PT12-S5	0.16	-1.77
PT12-S6	0.31	2.46

$$u(C_{ref}) = \frac{\sum_i u(C_{ref})_i}{n_R}$$

$$= \frac{3.0}{9}$$

$$= 0.33\%$$

$$RMS_{bias} = \sqrt{\frac{\sum (bias_i)^2}{n}}$$

$$= \sqrt{\frac{97.7}{9}}$$

$$= 3.30\%$$

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Analysis of Nickel in drinking water

Bias

- Bias contribution to overall uncertainty:
  - Bias:

    $\%RMS_{Bias} = 3.30\%$
  - Uncertainty of Reference value:

    $\%u_{Cref} = 0.33\%$

$$u_{bias} = \sqrt{RMS_{bias}^2 + u(C_{ref})^2}$$

$$= \sqrt{(3.30)^2 + (0.33)^2}$$

$$= 3.32\%$$

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Analysis of Nickel in drinking water

- ✓ Combined Standard uncertainty
  - ✓ Reproducibility: $\%R_w = 5.26\%$
  - ✓ Method and Laboratory bias: $\%u_{bias} = 3.32\%$

$$\%u_c = \sqrt{(5.26)^2 + (3.32)^2} = 6.22\%$$

- ✓ Expanded Uncertainty
  - ✓ Assume k=2, degrees of freedom > 30

$$U = k \times u_c = 12.4\%$$

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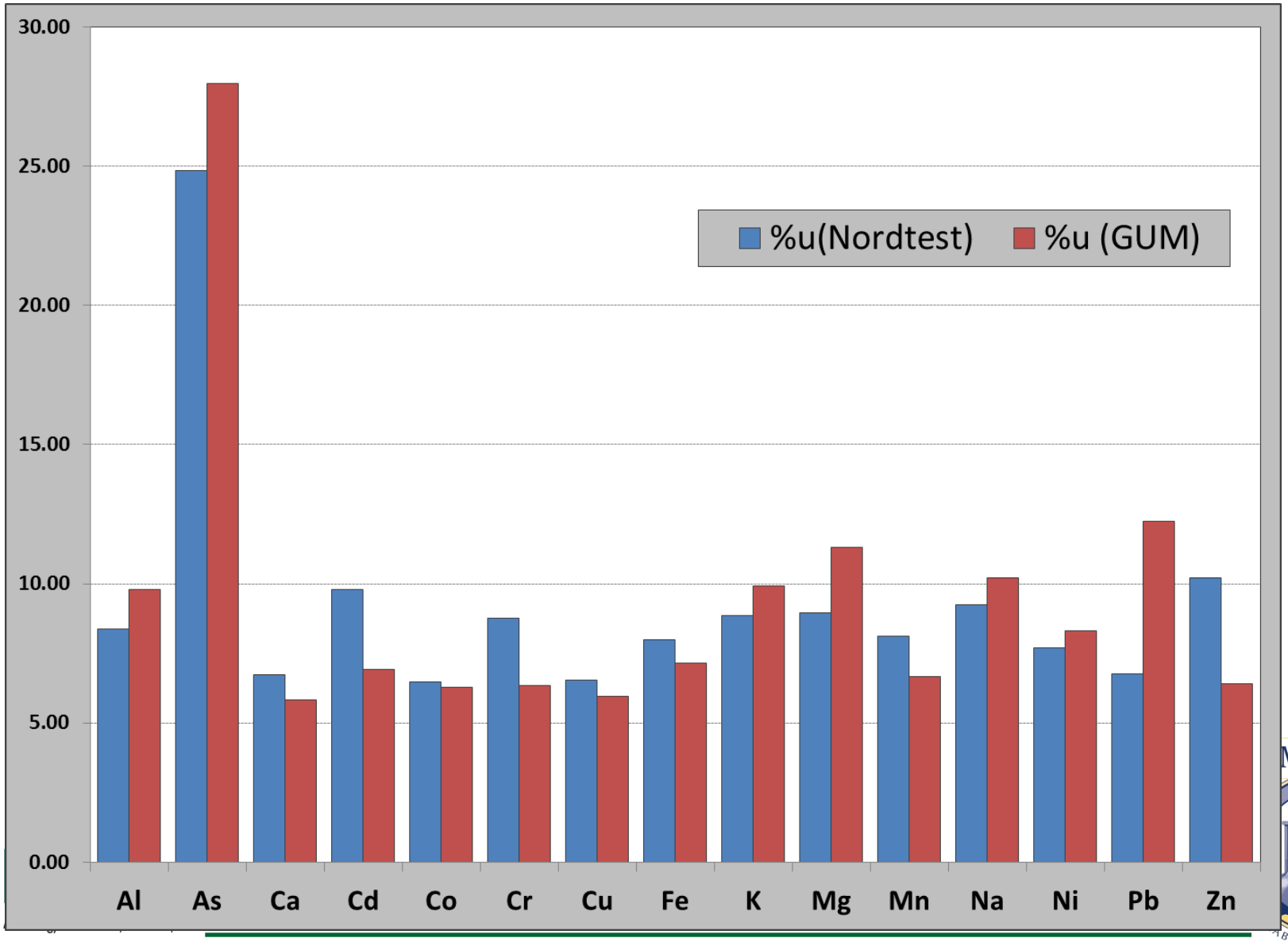
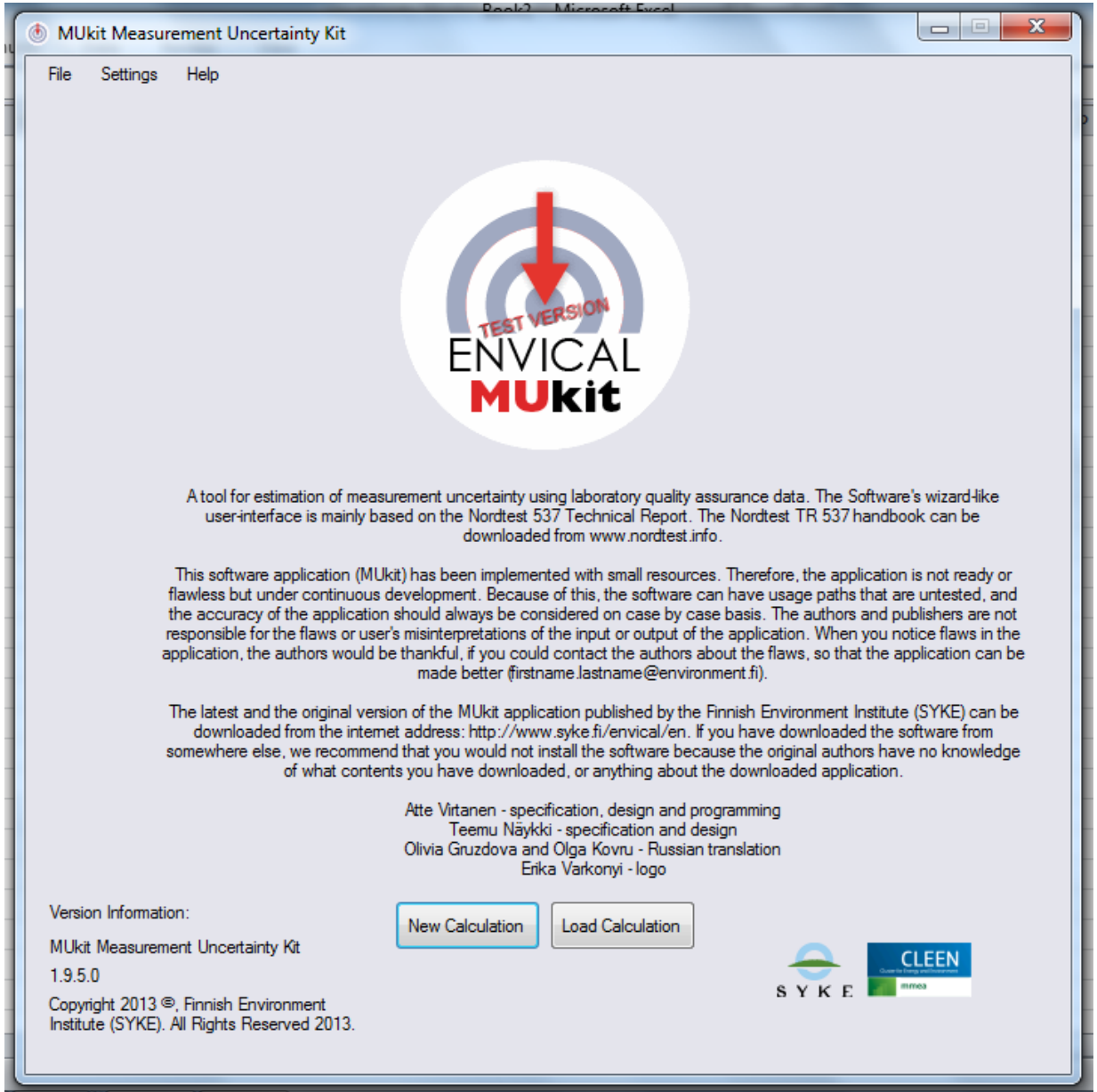
Analysis of trace elements in drinking water



Nordtest - MU Kit



NORDTEST: Example 2

Analysis of Cd in aqua regia extract of soil

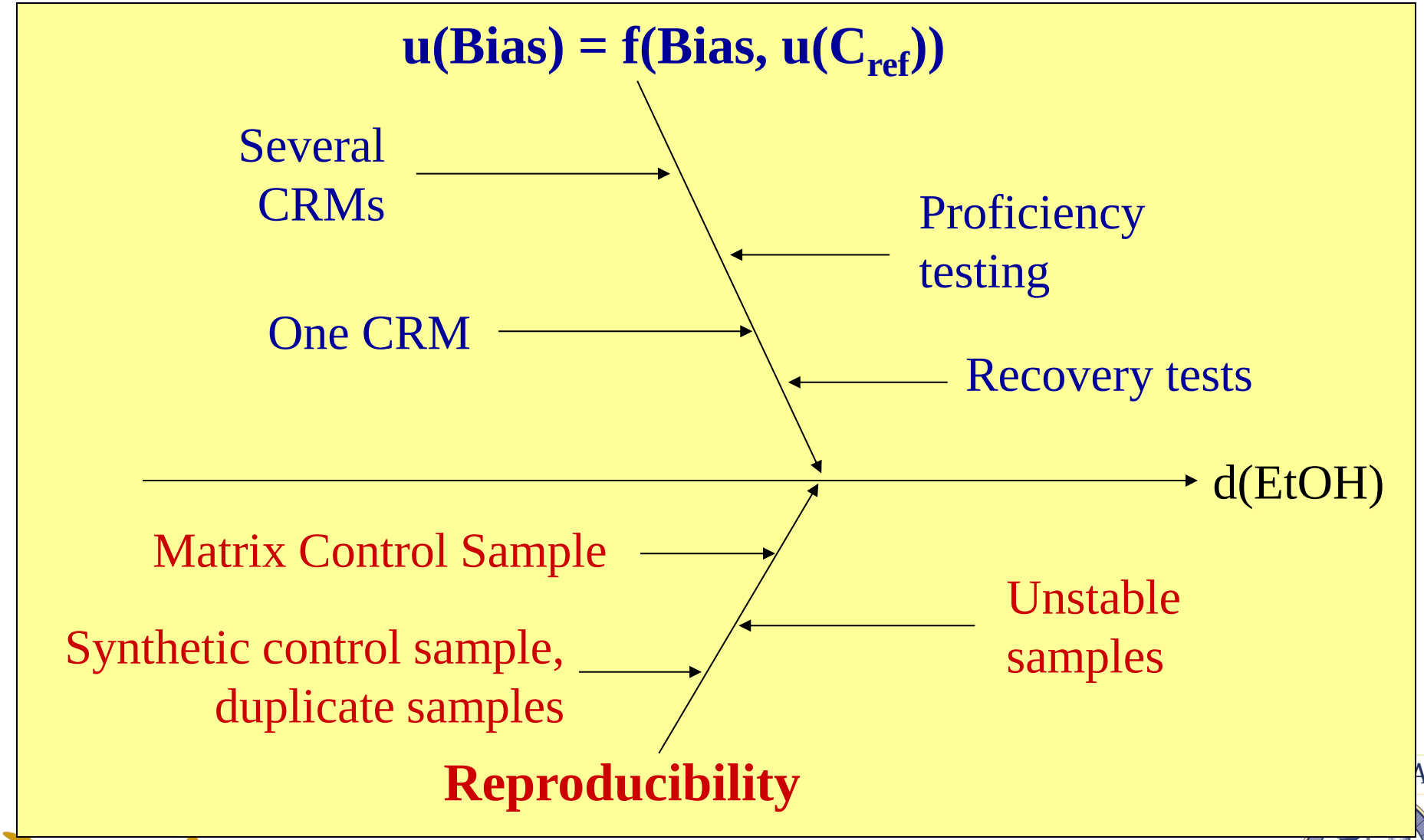
The laboratory has a X control chart for routine analysis of Cd in soil using a real soil sample.
From 30 measurements of the control sample:

Mean = 0.41 mg/kg
Standard deviation = 0.04 mg/kg.

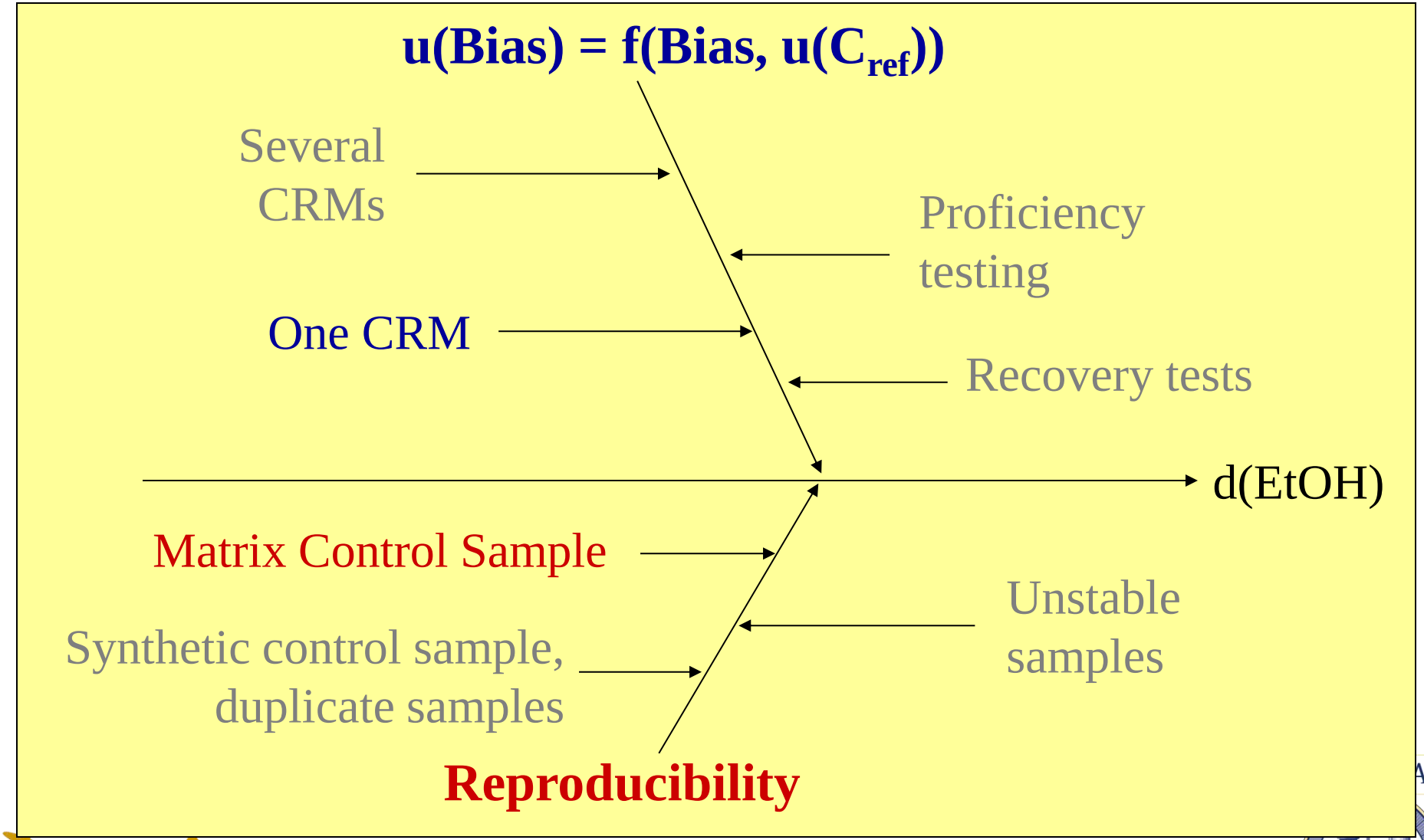
BCR-142R (light sandy soil CRM) was analysed during method validation, with the following results obtained:

No.	BCR142R Results (mg/kg)
1	0.231
2	0.245
3	0.256
4	0.224
5	0.229
6	0.241
7	0.221
8	0.230
9	0.222
10	0.238

Nordtest – approach: Cd in Soil

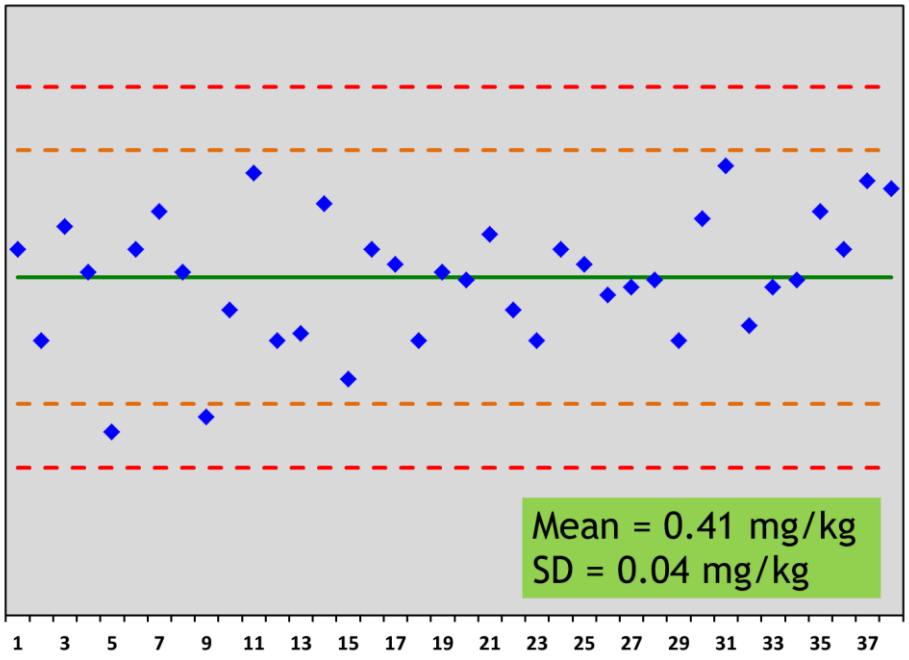


Nordtest – approach: Cd in Soil



Analysis of Cd in aqua regia extract of soil

- ✓ Within laboratory reproducibility, s_{Rw}
  - ✓ Control sample covering the whole analytical process:
    - ✓ Mean = 0.41 mg/kg
    - ✓ Standard deviation = 0.04 mg/kg



$$\%s_{R_w} = \frac{SD}{\bar{x}} \times 100$$

$$= \frac{0.04}{0.41} \times 100$$

$$= 9.76\%$$

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Analysis of Cd in aqua regia extract of soil

- ✓ Method and Laboratory bias: u_{bias}
  - ✓ Use of one certified reference material

$$u_{bias} = \sqrt{(bias)^2 + \left(\frac{s_{bias}}{\sqrt{n}}\right)^2 + u(C_{ref})^2}$$

$$\bar{x} = 0.2337 mg/kg$$

$$s_{bias} = 0.01122 mg/kg$$

$$\%s_{bias} = \frac{0.01122}{0.2337} \times 100 = 4.80\%$$

No.	BCR142R Results (mg/kg)
1	0.231
2	0.245
3	0.256
4	0.224
5	0.229
6	0.241
7	0.221
8	0.230
9	0.222
10	0.238

Analysis of Cd in aqua regia extract of soil

- ✓ Method and Laboratory bias: u_{bias}
  - ✓ Use of one certified reference material

$$u_{bias} = \sqrt{(bias)^2 + \left(\frac{s_{bias}}{\sqrt{n}}\right)^2 + u(C_{ref})^2}$$

- ✓ Bias:
  - ✓ Certificate of analysis

BCR-142R

$$\mu = 0.249 mg/kg$$

$$\bar{x} = 0.2337 mg/kg$$

$$\%Bias = \frac{0.2337 - 0.249}{0.249} \times 100 = -6.14\%$$

No.	BCR142R Results (mg/kg)
1	0.231
2	0.245
3	0.256
4	0.224
5	0.229
6	0.241
7	0.221
8	0.230
9	0.222
10	0.238

Analysis of Cd in aqua regia extract of soil

- ✓ Method and Laboratory bias: u_{bias}
  - ✓ Use of one certified reference material

$$u_{bias} = \sqrt{(bias)^2 + \left(\frac{s_{bias}}{\sqrt{n}}\right)^2 + u(C_{ref})^2}$$

- ✓ $u(C_{ref})$:
  - ✓ Certificate of analysis

BCR-142R

$$\mu = 0.249 mg/kg$$

$$u(C_{ref}) = 0.010 / 3.18 = 0.00314 mg/kg$$

$$\%u(C_{ref}) = \frac{0.00314}{0.249} \times 100 = 1.263\%$$

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Analysis of Cd in aqua regia extract of soil

- ✓ Method and Laboratory bias: u_{bias}
  - ✓ Use of one certified reference material

$$u_{bias} = \sqrt{(bias)^2 + \left(\frac{s_{bias}}{\sqrt{n}}\right)^2 + u(C_{ref})^2}$$

$$= \sqrt{(-6.14)^2 + \left(\frac{4.80}{\sqrt{10}}\right)^2 + (1.263)^2} = 6.45\%$$

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Analysis of Cd in aqua regia extract of soil

- ✓ Combined Standard uncertainty
  - ✓ Reproducibility: $\%R_w$ = *9.76%*
  - ✓ Method and Laboratory bias: $\%u_{bias}$ = *6.45%*

$$\%u_c = \sqrt{(9.76)^2 + (6.45)^2} = 11.70\%$$

- ✓ Expanded Uncertainty
  - ✓ Assume k=2, degrees of freedom > 30

$$U = k \times u_c = 23.4\%$$

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NORDTEST: Example 3

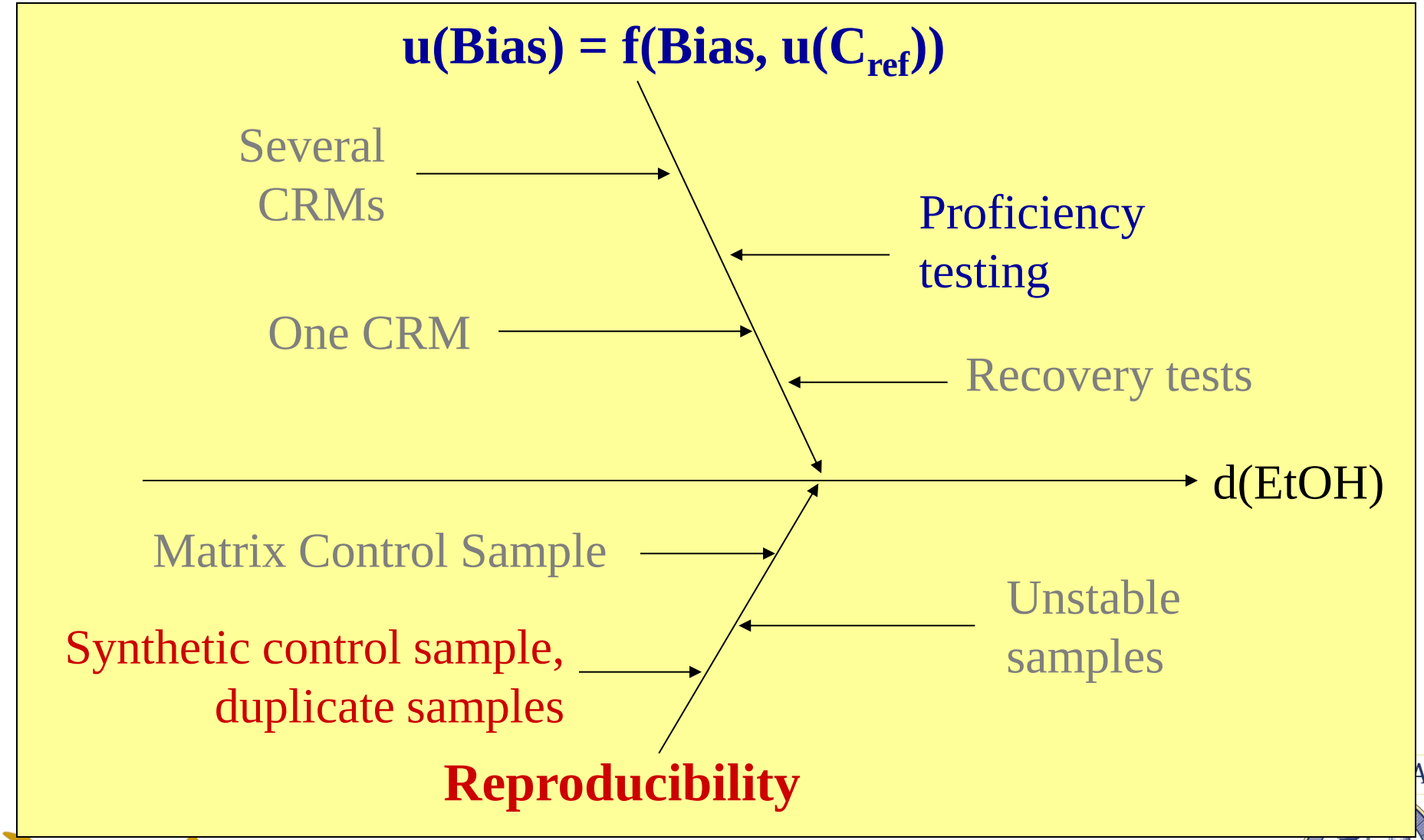
Analysis of Nitrate-N in waste water

A laboratory routinely analyses a standard nitrate quality control solution.

Duplicate analysis of real waste water samples are used to construct a range control chart.

The laboratory doesn't have a CRM, but participates in a PT scheme on nitrate in waste water.

Nordtest – approach: Nitrate-N



Analysis of Nitrate-N in waste water

Reproducibility

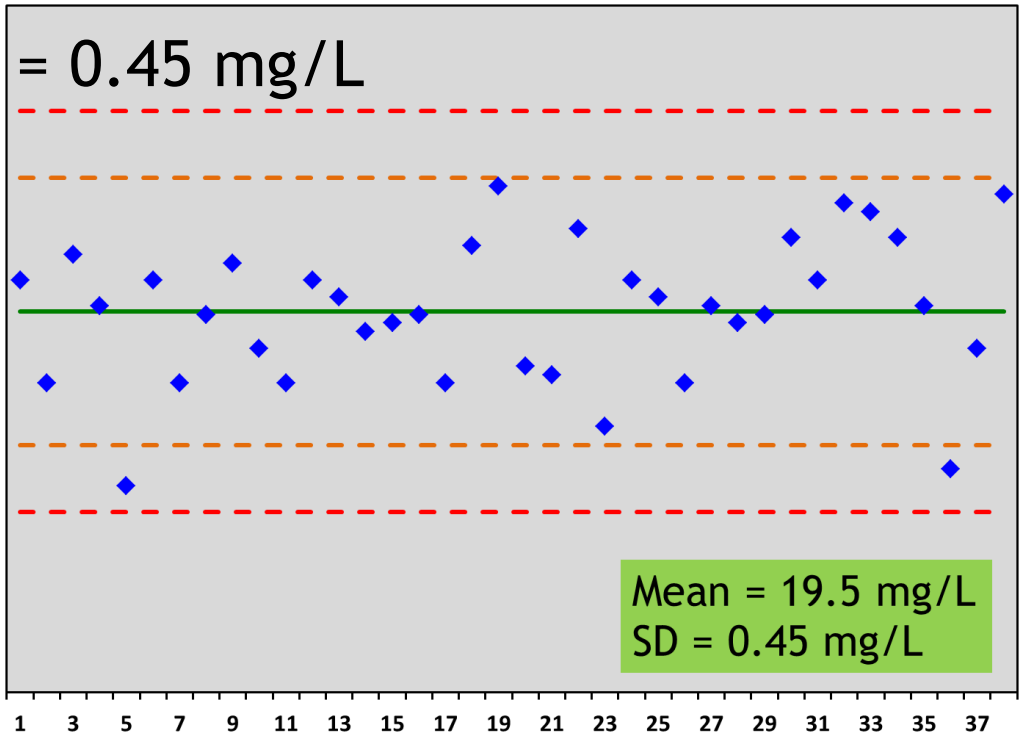
The laboratory routinely analyse a standard nitrate quality control solution:

- ✓ Concentration = 20 mg/l nitrate-N.
- ✓ From 40 measurements of the solution:
  - ✓ Mean = 19.5 mg/L
  - ✓ Standard deviation = 0.45 mg/L

$$\%s_{R_w} = \frac{SD}{\bar{x}} \times 100$$

$$= \frac{0.45}{19.5} \times 100$$

$$= 2.31\%$$



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Analysis of Nitrate-N in waste water

Reproducibility

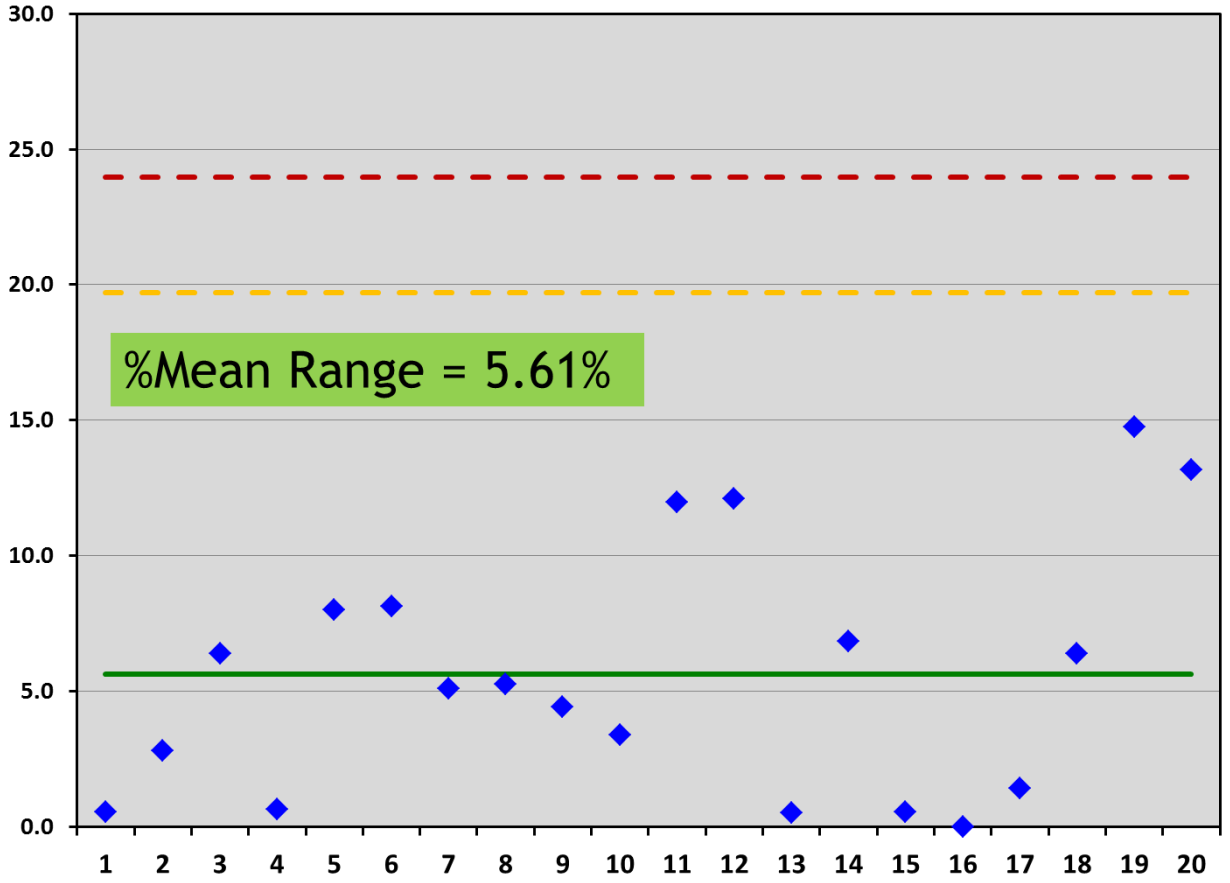
Duplicate analysis of real waste water samples gives a range control chart with the following data:

Rpt No	x(1)	x(2)	Rpt No	x(1)	x(2)
1	18.3	18.4	11	16.5	18.6
2	25.3	24.6	12	17.1	19.3
3	15.2	16.2	13	20.1	20.2
4	32.3	32.1	14	11.3	12.1
5	14.4	15.6	15	18.7	18.8
6	20.1	21.8	16	19.2	19.2
7	15.3	16.1	17	21.3	21.6
8	14.8	15.6	18	27.3	29.1
9	19.9	20.8	19	29.1	25.1
10	32.1	33.2	20	14.2	16.2

Analysis of Nitrate-N in waste water

Reproducibility

Duplicate analysis of real waste water samples gives a range control chart with the following data:



$$\%s_{r_w} = \frac{\%MeanRange}{d_2}$$

$$= \frac{5.60}{1.128}$$

$$= 4.96\%$$

Analysis of Nitrate-N in waste water

Reproducibility

- ✓ Reproducibility contribution to overall uncertainty:
  - ✓ Mean control Chart: $\%s_{Rw} = 2.31\%$
  - ✓ Range control Chart: $\%s_{rw} = 4.96\%$

$$\%S_R = \sqrt{(2.31)^2 + (4.96\%)^2} = 5.47\%$$

Analysis of Nitrate-N in waste water

Bias

The laboratory doesn't have a CRM, but participates in a PT scheme on nitrate in waste water with the following results (all values in mg/l N):

PT no.	Assigned value (median)	Reproducibility SD	No. Participants	Lab result
L19 - 1	7.532	0.257	62	7.47
L19 - 2	28.31	1.026	61	28.2
L19 - 3	37.67	1.481	62	37.4
L14 - 1	7.967	0.320	37	8.18
L14 - 2	13.58	0.549	37	13.5
L14 - 3	35.73	1.026	36	35.8

$$u(C_{ref})_i = 1{,}25 \cdot \frac{s_{R,i}}{\sqrt{n_{T,i}}}$$

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Analysis of Nitrate-N in waste water

Bias

The laboratory doesn't have a CRM, but participates in a PT scheme on nitrate in waste water with the following results (all values in mg/l N):

PT No.	s_R (%)	%u(C_{ref})	%Bias
L19-1	3.41	0.54	0.82
L19-2	3.62	0.58	0.39
L19-3	3.93	0.62	0.72
L14-1	4.02	0.83	-2.67
L14-2	4.04	0.83	0.59
L14-3	2.87	0.60	-0.20

$$RMS_{bias} = \sqrt{\frac{\sum (bias_i)^2}{n}} = 1.22\%$$

$$u(C_{ref})_i = 1{,}25 \cdot \frac{s_{R,i}}{\sqrt{n_{T,i}}}$$

$$u(C_{ref}) = \frac{\sum_i u(C_{ref})_i}{n_R} = 0.67\%$$

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Analysis of Nitrate-N in waste water

Bias

- ✓ Bias contribution to overall uncertainty:
  - ✓ Bias:

    $\%RMS_{Bias} = 1.22\%$
  - ✓ Uncertainty of Reference value:

    $\%u_{Cref} = 0.67\%$

$$u_{bias} = \sqrt{RMS_{bias}^2 + u(C_{ref})^2}$$

$$= \sqrt{(1.22)^2 + (0.67)^2}$$

$$= 1.39\%$$

Analysis of Nitrate-N in waste water

- ✓ Combined Standard uncertainty
  - ✓ Reproducibility: $\%R_w = 5.47\%$
  - ✓ Method and Laboratory bias: $\%u_{bias} = 1.39\%$

$$\%u_c = \sqrt{(5.47)^2 + (1.39)^2} = 5.64\%$$

- ✓ Expanded Uncertainty
  - ✓ Assume k=2, degrees of freedom > 30

$$U = k \times u_c = 11.3\%$$

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