The bias component in measurement uncertainty

EURACHEM Workshop on Validation/Traceability/Measurement Uncertainty
Challenges for the 21st Century's analysis

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- Laboratory and method bias
- Eurachem view on uncertainty
- Estimation of uncertainty including bias uncertainty
  - From demands – EU directive
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    - How many measurements
    - Example – SiO_2 in cement
- Citation from GUM
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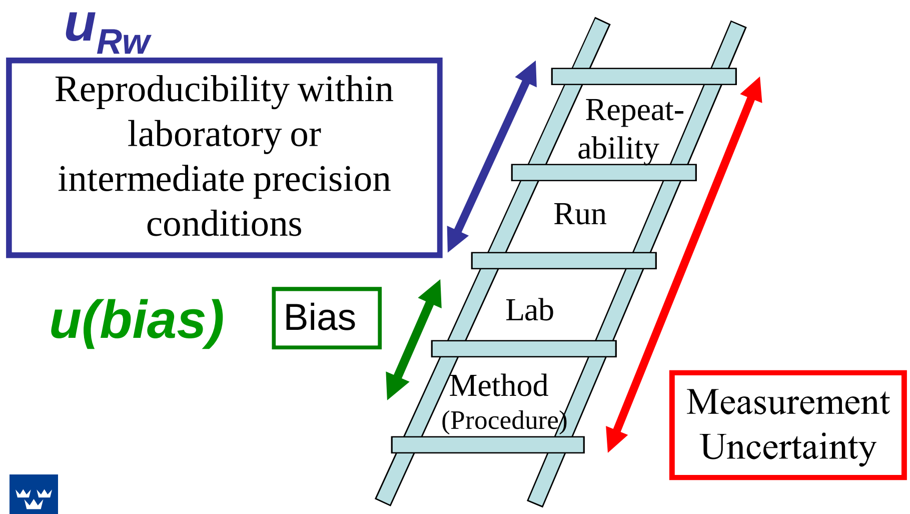
Ladder of errors in ONE laboratory



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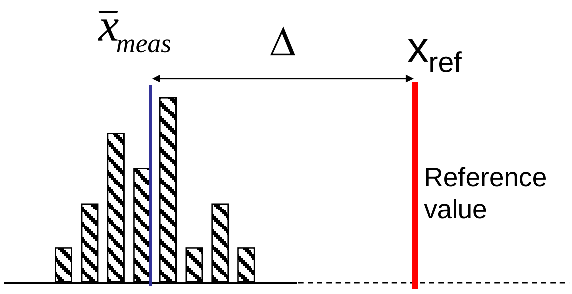
Measurement bias



Within the scope of the method (procedure) we may have several bias estimates over the concentration interval and from different sample types

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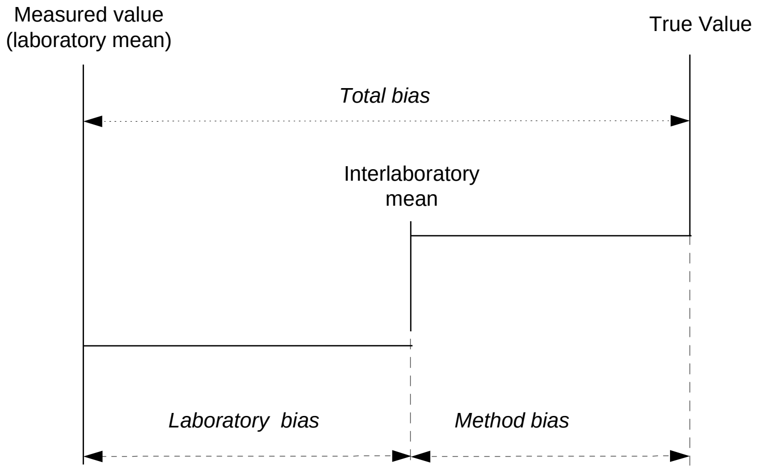
Laboratory and method bias



Note: Laboratory and method biases are shown here acting in the same direction. In reality this is not always the case.

Figure from Eurachem ”Validation” guide

Bias in Eurachem guide on uncertainty (2012)

3.1.3 Bias should be shown to be *negligible or corrected for*, but in either case the uncertainty associated with the determination of the bias remains an essential component of overall uncertainty.

3.2.7. In carrying out studies of overall bias, it is important that the reference materials and values are relevant to the materials under routine test.

5.4 …method used is empirical. It is not meaningful to consider correction for bias intrinsic to the method, since the measurand is defined by the method used.

6.6. In practice, it is more usual in analytical measurement to consider uncertainties associated with elements of overall method performance, such as observable precision and bias measured with respect to appropriate reference materials.

Bias in Eurachem guide on uncertainty (2012)

7.2.3 Section 7.16. covers the treatment of known bias in uncertainty estimation.

7.6.1 Where the **bias* itself**, the **uncertainty in the reference values** used, and the **precision associated with the bias check**, are all small compared to *sR*, no additional allowance need be made for bias uncertainty.

*referring to method bias

7.16 Where the bias is not significant compared to the combined uncertainty, the bias may be neglected.

iv) Where the bias is significant compared to the combined uncertainty, additional action is required. Appropriate actions might:

• Eliminate or correct for the bias, making due allowance for the uncertainty of the correction.

• Report the observed bias and its uncertainty in addition to the result.

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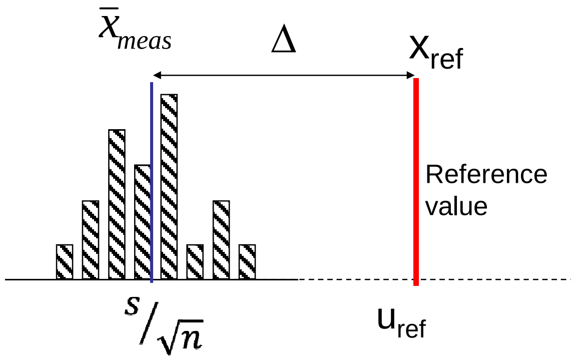
Estimation bias contribution – three terms

1. bias* itself,
2. the uncertainty in the reference values used,
3. the precision associated with the bias check



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To correct or not correct for bias?

From VIM on Measurement Uncertainty
"NOTE 1 Measurement uncertainty includes components arising from systematic effects, such as components associated with corrections and the assigned quantity values of measurement standards, as well as the definitional uncertainty.

Sometimes estimated systematic effects are not corrected for but, instead, associated measurement uncertainty components are incorporated"

We have a component b accounting for bias Nordtest TR537 uses u(bias). I will present one of several possible ways to estimate this b component

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Estimation of measurement uncertainty including bias uncertainty

Uncertainty, ***u*** is estimated as a root sum of squares of

- a standard deviation ***s*** characterising the (im)precision of the measurement and an
- estimate ***b*** *as a standard uncertainty* **accounting** for measurement bias

$$u = \sqrt{s^2 + b^2}$$

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Estimation of measurement uncertainty including bias uncertainty

Using information on s_{Rw} (within lab reproducibility) and information about the bias component ***b* accounting** for measurement bias within the **scope of the method** measurement uncertainty can be estimated

1. Based on requirements on s_{Rw} *and bias*
   - EU directive
2. Based on measurement
   - (Internal Quality control)
   - **Bias measurement**
     - **One reference**
     - **Several references**

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Estimation of measurement uncertainty based on requirements in the EU directive

Extract from Annex III of the EU drinking water directive (1998)

Parameter	Parametric value	Trueness % of parametric value (Note 1)	Precision % of parametric value (Note 2)
Ammonium	0.5 mg L^{-1}	10	10
Arsenic	10 µg L^{-1}	10	10
Mercury	1 µg L^{-1}	20	10
Pesticides	0.5 µg L^{-1}	25	25

Note 1 (*): Trueness …is the difference between the mean value of the large number of repeated measurements and the true value.
Note 2 (*): Precision is …expressed as the standard deviation (within and between batch) of the spread of results about the mean. Acceptable precision is **twice** the relative standard deviation

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Estimation of measurement uncertainty based on requirements in the EU directive

$$u = \sqrt{s^2 + b^2}$$

$$u_{max} = \sqrt{\left(\frac{\text{limit}_{\text{precision}}}{2}\right)^2 + \left(\frac{\text{limit}_{\text{trueness}}}{\sqrt{3}}\right)^2}$$

If we assume that the value for trueness is the maximum allowed bias, then the standard uncertainty component can be calculated from the standard deviation of a rectangular distribution, which is the half width of the interval divided by root of 3.

B. Magnusson and M. Koch, Measurement Quality in Water Analysis. In: Peter Wilderer (ed.) Treatise on Water Science, vol. 3, pp. 153–169 Oxford: Academic Press. (2011)

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Estimation of measurement uncertainty based on requirements in the EU directive

Requirements in the EU drinking water directive as standard uncertainties and the estimated maximum standard and expanded measurement uncertainty. All requirements are given in percent of the parametric value.

Parameter	Parametric value	Trueness %	Precision %	Standard uncertainty %	Expanded uncertainty %
Ammonium	0.5 mg L^{-1}	5.8	5	7.6	15
Mercury	1 µg L^{-1}	11.5	5	13	25
Pesticides	0.5 µg L^{-1}	14.4	12.5	20	38

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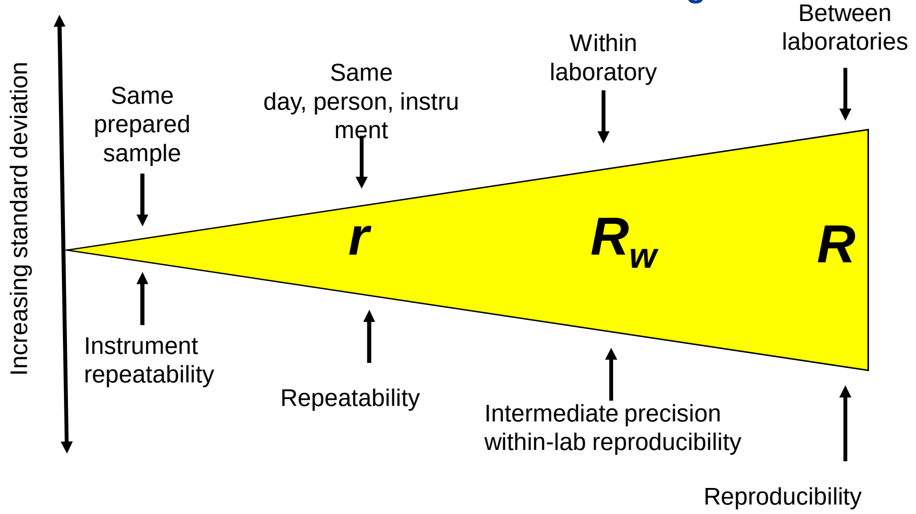
Measurement conditions for determining bias



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How many measurement of bias are needed?

Demand in the directive was a bias less than 10 % and a standard deviation of less than 5 %.

Number of measurement, *n*, needed to detect a bias, Δ with a method having the standard deviation, *s.*

Δ/s	0,5	0,6	0,8	1,0	**2,0**	3,0
n	55	39	23	16	**6**	4

(Data from NIST Special publication nr 829, 95 % confidence interval, the uncertainty of the reference valueis not taken into account)

Propose to make 6 measurments for each sample type at this concentration level under within-lab reproducibility conditions

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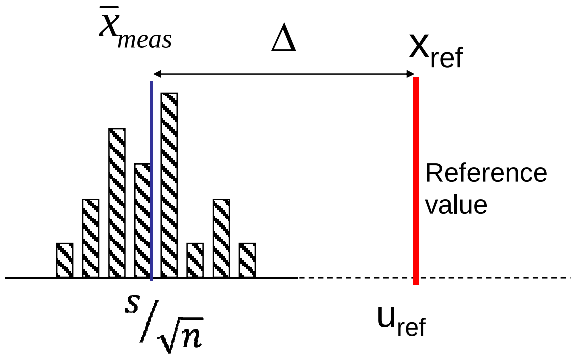
Mätosäkerhet och bias 2011-10-27 18

Estimation bias contribution – three terms

1. bias* itself,
2. the uncertainty in the reference values used,
3. the precision associated with the bias check



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Estimation of the bias contribution b accounting for measurement bias – one reference

The bias contribution, **b,** to uncertainty $u(y_{OBS})$ can be obtained by:

- the mean deviation,
- the uncertainty of the reference value
- the standard deviation of the mean value of the replicate measurements made in the bias investigation

$$b = \sqrt{\Delta^2 + \left(\frac{s}{\sqrt{n}}\right)^2 + u_{ref}^2}$$

$$U = k\sqrt{u(y_{OBS})^2 + b^2}$$

Other proposal are listen in

B Magnusson, S L R Ellison, Treatment of uncorrected measurement bias in uncertainty estimation for chemical measurements, Anal Bioanal Chem, , (2008) 390:201-213

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Different proposals to expand uncertainty

Correction not applied		
$U = k \cdot \sqrt{u(y_{obs})^2 + \Delta^2 + u_\Delta^2}$	RSSu	Lira & Wögler Nordtest NIST
$U = k\sqrt{u(y_{obs})^2 + \left(\frac{\Delta}{k}\right)^2 + u_\Delta^2}$	RSSU	IUPAC Barwick et al APHA
$U_+ = \max\left(0, k \cdot \sqrt{u(y_{obs})^2 + u_\Delta^2} - \Delta\right)$ $U_- = \max\left(0, k \cdot \sqrt{u(y_{obs})^2 + u_\Delta^2} + \Delta\right)$	SUMU	NIST
$U = k \cdot \sqrt{u(y_{obs})^2 + u_\Delta^2} + \lvert\Delta\rvert$	$SUMU_{MAX}$	IUPAC Maroto *et al.*
$U = k \cdot \sqrt{u(y_{obs})^2 + u_\Delta^2} + E\lvert\Delta\rvert$ where E is dependent on the bias and is in the range 0-2	U_e	Synek

Estimation of the bias contribution to measurement uncertainty – several references

The bias contribution, **b,** to measurement uncertainty is obtained from:

- the root mean square of the deviations,
- the root mean square of the references values
- the standard deviation of the mean values of the replicate measurements made in the bias investigation. However this term will normally be negligible.

$$b = \sqrt{RMS_{bias}^{\;2} + RMS_{u\,ref}^{\;2}}$$

Example: SiO_2 in cement short summary

Calculate expanded uncertainty U = 2 * u_c

u_c - within-lab reproducibility + bias contribution

- **within-lab reproducibility(Rw) *s=u(Rw)* = 0,15 % SiO_2**
- **from several CRM *b* = 0,16 % SiO_2**

$$u_c = \sqrt{u(R_w)^2 + b^2} =$$

$$= \sqrt{0{,}15^2 + 0{,}16^2} = 0{,}22\,\%$$

$$U = 2 \cdot u_c = 2 \cdot 0.22 = 0{,}44 \approx 0.5\%\ \mathrm{SiO_2}$$

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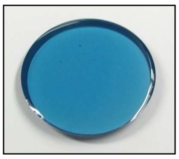
Determinaton of SiO_2 in cement

Specify measurand

- **Total concentration of silicon reported as silicon dioxide. Range 15-25 %**
- **Describe the analytical process in steps**
  - **Silicon is measured with XRF sample preparation - lithium tetraborate bead**
  - **XRF instrumentet is calibrated with pure oxides Ca, Si, K, Fe…using theoretical alfa correction**
- **Customer demand on measurement uncertainty (95 %): at a level of 20 % is ± 0,5 % SiO_2**



XRF – X-Ray Fluorescence
CRM = Certified Reference Material

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Estimate *b* accounting for measurement bias - RMSbias

CRM	Certified values x_{ref}	Measurement uncertainty (95 %)	Measured mean value*	Bias
	% SiO_2	% SiO_2	% SiO_2	% SiO_2
NIST1881	22,71	0,10	22,82	**0,11**
NIST1885	21,40	0,12	21,28	**-0,12**
NIST1886	22,92	0,12	22,70	**-0,22**
NIST1887	20,28	0,12	20,22	**-0,06**
BCR354	21,80	0,28	21,68	**-0,12**
			Mean	**-0,08**
			RMS_{bias}	**0,14**

* Measured 6 different days

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Estimate *b* accounting for measurement bias - RMSbias

$$bias_i = \bar{x}_{meas.} - x_{ref}$$

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

$$= \sqrt{\frac{(+0{,}11^2) + (-0{,}12^2) + \ldots(-0{,}12^2)}{n}} = 0{,}14\,\%\,(abs)$$

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Estimate b accounting for measurement bias - RMS u_{ref}

CRM	Certified value x_{ref}	Measurement uncertainty (95 %)
	%	%
NIST1881	22,71	0,10
NIST1885	21,40	0,12
NIST1886	22,92	0,12
NIST1887	20,28	0,12
BCR354	21,80	0,28
Mean		0,14
RMS Uref		0,16

$$RMS\, uref = \\ = \frac{0,16}{2} = \\ = 0,08\,\%$$

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Estimation of the bias contribution to measurement uncertainty – several references

$$b = \sqrt{RMS_{bias}{}^2 + RMS\, u_{ref}{}^2}$$

$$= \sqrt{0.14^2 + 0.08^2} = 0.16\%$$

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Estimation of uncertainty - determination of SiO_2 in cement

Calculate expanded uncertainty U = 2 * u_c

u_c - within-lab reproducibility + bias components

- **within-lab reproducibility(Rw) s=u(Rw) = 0,15 % SiO_2**
- **from several CRM b = 0,16 % SiO_2**

$$u_c = \sqrt{u(R_w)^2 + b^2} =$$

$$= \sqrt{0{,}15^2 + 0{,}16^2} = 0{,}22\,\%$$

$$U = 2 \cdot u_c = 2 \cdot 0.22 = 0{,}44 \approx 0.5\%\ SiO_2$$

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Some thoughts from the GUM – 3.4.8

Although this *Guide* provides a framework for assessing uncertainty, it cannot substitute for critical thinking, intellectual honesty and professional skill.

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.

The quality and utility of the uncertainty quoted for the result of a measurement therefore ultimately depend on the understanding, critical analysis, and integrity of those who contribute to the assignment of its value

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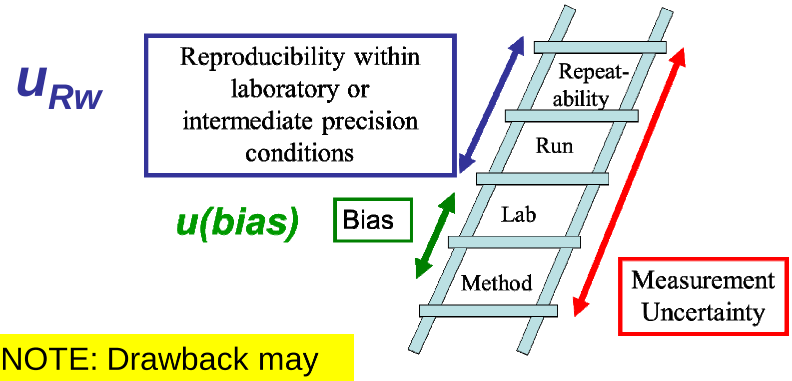
Estimation of measurement uncertainty - Important to consider the uncertainty of any possible remaining bias within the scope of the method



NOTE: Drawback may be too high uncertainty.