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Evaluation of the measurement uncertainty based on in-house validation data

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Workshop:
Quality Assurance Challenges of Measurements from Field to Laboratory with a Focus on ISO/IEC 17025:2017 Requirements

(D)

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Outline

Different approaches for MU evaluation

Uncertainty components

Available guidance

Need for additional guidance

Snapshots of the guide

Final remarks

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Different approaches for MU evaluation

- Bottom-up approach
- Top-down approach
  - Based on in-house validation data
  - Based on interlaboratory data

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Different approaches for MU evaluation

- Bottom-up approach
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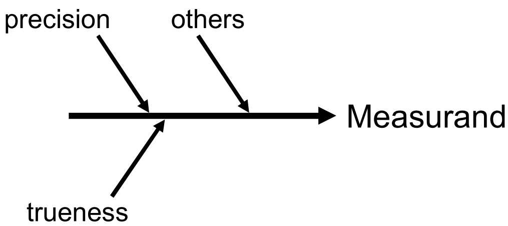
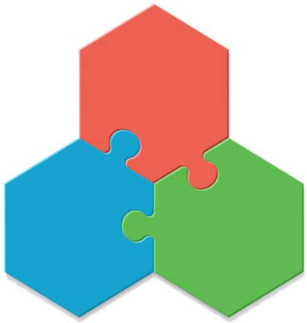
Uncertainty components

- Precision
- Trueness
- Others





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Available guides
Using in-house validation data for MU evaluation

- VAM project, 2000 [1]
- Eurachem/CITAC, QUAM, 2012 (Example A4) [2]
- Eurolab TR 1/2007, 2007 [3]
- Nordtest TR 537, 2017 [4]

1. V. J. Barwick, S. L. R. Ellison. VAM Project 3.2.1: Development and Harmonisation of Measurement Uncertainty Principles, LGC, 2000.
2. S. L. R. Ellison, A. Williams (Eds). Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement, Third edition, 2012.
3. Eurolab, Measurement uncertainty revisited: Alternative approaches to uncertainty evaluation, Technical Report No. 1/2007, 2007.
4. B. Magnusson, T. Näykki, H. Hovind, M. Krysell, E. Sahlin, Handbook for calculation of measurement uncertainty in environmental laboratories (NT TR 537 – Edition 4), 2017.

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Need for additional guidance

- How to handle the variation of the MU with the concentration
- How to quantify precision improvement from replicate analysis under different conditions
- How to handle systematic effects estimated from the analysis of various reference materials:
    - Correct/ Not correct
    - Systematic effects variation with sample matrix

7

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Guide presented as a tutorial where options are explained!

8

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Snapshots of the guide (1)

How to handle the variation of the MU with the concentration, c

9

9

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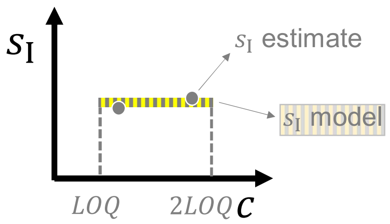
Snapshots of the guide (1)

How to handle the variation of the MU with the concentration, c

Below about 2*LOQ*, the absolute intermediate precision, s_{I} , is approximately constant.



LOQ – limit of quantification

10

10

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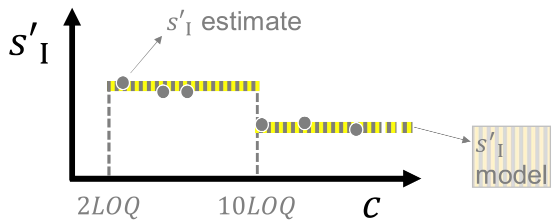
Snapshots of the guide (1)

How to handle the variation of the MU with the concentration, c

Below about 2*LOQ*, the absolute intermediate precision, s_{I} , is approximately constant.

Above about 2*LOQ*, the relative intermediate precision, $s'_{\mathrm{I}}(s'_{\mathrm{I}} = s_{\mathrm{I}}/c)$, is approximately constant.



LOQ – limit of quantification

11

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Snapshots of the guide (1)

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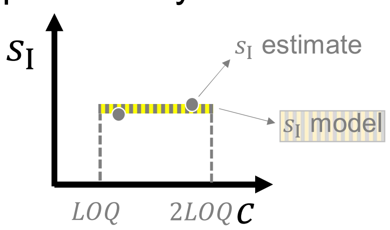

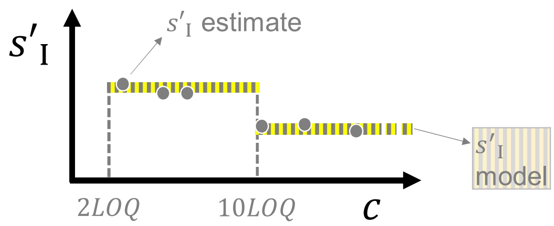

LOQ – limit of quantification

12

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Snapshots of the guide (2)

How precision improves from replicate analysis

13

13

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Snapshots of the guide (2)

How precision improves from replicate analysis

Sample result can be estimated as **mean of replicate results** obtained under:

- repeatability conditions
- intermediate precision conditions

14

14

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Snapshots of the guide (2)

How precision improves from replicate analysis

Sample result can be estimated as **mean of replicate results** obtained under:

- ◦ repeatability conditions
- ◦ intermediate precision conditions

Validation data: • Intermediate precision standard deviation: s_{I}
• Repeatability standard deviation: s_{r}

15

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Snapshots of the guide (2)

How precision improves from replicate analysis

If replicates are in agreement with quantified imprecision…

Example: duplicates under repeatability conditions, x_1 and x_2 :

$$|x_1 - x_2| \leq 2.8s_{\mathrm{r}}$$

(…)

16

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Snapshots of the guide (2)

How precision improves from replicate analysis

If replicates are in agreement with quantified imprecision…

Example: duplicates under repeatability conditions, x_1 and x_2 :

$$|x_1 - x_2| \leq 2.8 s_\mathrm{r}$$

Precision standard uncertainty, u_P

Single Analysis	Mean of *n* replicates obtained on different days (dd)	Mean of *n* replicates obtained on the same day (sd)
$u_\mathrm{P} = s_\mathrm{I}$	$u_\mathrm{P}(n; \mathrm{dd}) = \frac{s_\mathrm{I}}{\sqrt{n}}$	$u_\mathrm{P}(n; \mathrm{sd}) = \sqrt{s_\mathrm{I}^2 + \frac{s_\mathrm{r}^2(1-n)}{n}}$

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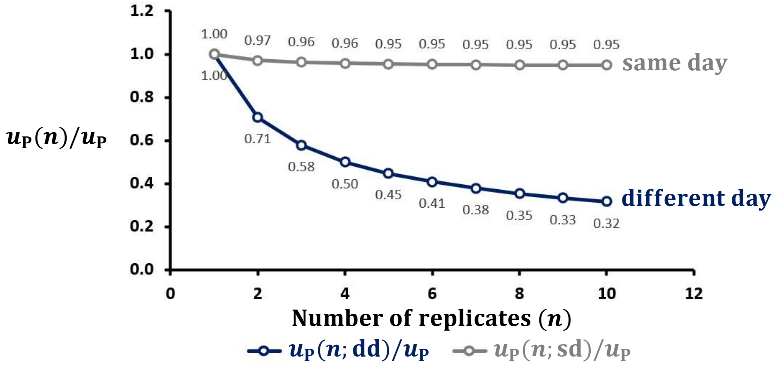
Snapshots of the guide (2)

Single Analysis, u_P	Mean of *n* replicates obtained on different days (dd), $u_\mathrm{P}(n; \mathrm{dd})$	Mean of *n* replicates obtained on the same day (sd), $u_\mathrm{P}(n; \mathrm{sd})$

Precision reduction from replicate analysis if $s'_\mathrm{I} / s'_\mathrm{r} = 3$:



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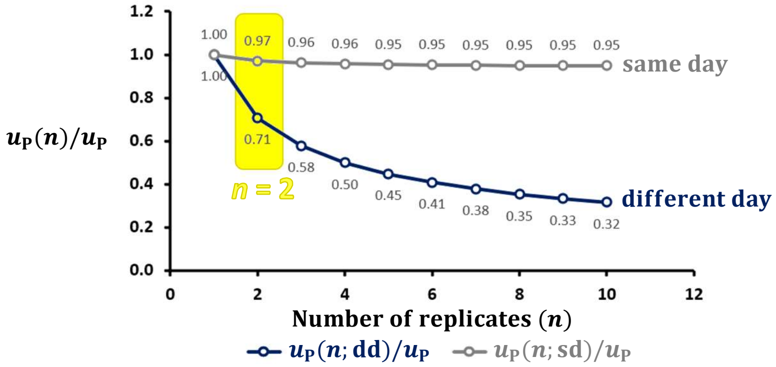
Snapshots of the guide (2)

Single Analysis, u_{P}	Mean of *n* replicates obtained on different days (dd), $u_{\mathrm{P}}(n;\mathrm{dd})$	Mean of *n* replicates obtained on the same day (sd), $u_{\mathrm{P}}(n;\mathrm{sd})$

Precision reduction from replicate analysis if $s'_{\mathrm{I}}/\ s'_{\mathrm{r}} = 3$:



19

19

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Snapshots of the guide (2)

20

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Snapshots of the guide (2)

Trueness uncertainty assessed from *N* reference materials

Evaluated through the determination of analyte recovery:

$$\frac{c}{c_{\mathrm{Ref}}}$$

Recovery value is fit for results correction if systematic effects are proportional to the concentration.

21

21

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Snapshots of the guide (2)

Trueness uncertainty assessed from *N* reference materials

After recovery corrections has been made:

$$u_{\bar{R}} = \frac{\sqrt{\sum_{i=1}^{N}\left\{\bar{R}_i^2\left[\frac{s_{\mathrm{I}}^2(R_i)}{\bar{R}_i^2 \cdot n_i} + \frac{u^2\left(c_{\mathrm{Ref}(i)}\right)}{c_{\mathrm{Ref}(i)}^2}\right]\right\}}}{N}$$

22

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Snapshots of the guide (2)

Trueness uncertainty assessed from *N* reference materials

After recovery corrections has been made :

$$u_{\bar{R}} = \frac{\sqrt{\sum_{i=1}^{N}\left\{\bar{R}_i^2\left[\frac{s_{\mathrm{I}}^2(R_i)}{\bar{R}_i^2 \cdot n_i} + \frac{u^2\left(c_{\mathrm{Ref}(i)}\right)}{c_{\mathrm{Ref}(i)}^2}\right]\right\}}}{N}$$

i^{th} mean recovery

recovery variance (interm. pres.)

square of the relative standard uncertainty of the i^{th} reference value

number of i^{th} recovery tests

23

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Snapshots of the guide (2)

Trueness uncertainty assessed from *N* reference materials

After recovery corrections has been made :

R1-CRM1	R2-CRM2	R3-PT1	R4-SPK1	R5-SPK2
$c_{R1;1}$	$c_{R2;1}$	$c_{R3;1}$	$c_{R4;1}$	$c_{R5;1}$
$c_{R1;2}$		$c_{R3;2}$	(…)	$c_{R5;2}$
$c_{R1;3}$			$c_{R4;11}$	$c_{R5;3}$
$T_1 =$	T_2	T_3	$T_4 =$	T_3

Different day

$T_1 = \bar{R}_{R1}^2\left[\frac{s_{\mathrm{I}}^2(R_{R1})}{\bar{R}_{R1}^2 \cdot 3} + \frac{u^2\left(c_{\mathrm{Ref(R1)}}\right)}{c_{\mathrm{Ref(R1)}}^2}\right]$

$T_4 = \bar{R}_{R4}^2\left[\frac{s_{\mathrm{I}}^2(R_{R4})}{\bar{R}_{R4}^2 \cdot 11} + \frac{u^2\left(c_{\mathrm{Ref(R4)}}\right)}{c_{\mathrm{Ref(R4)}}^2}\right]$

$$u_{\bar{R}} = \frac{\sqrt{\sum_{i=1}^{5}\{T_i\}}}{5}$$

24

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FINAL REMARKS

Additional guidance on using in-house validation data for MU evaluation is needed

The simplification of MU evaluation involves facing some challenges properly

25

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Online Eurachem/CITAC Workshop on:

Measurement uncertainty evaluation based on in-house validation data

Dates: 25-26 October 2022

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26