Eurachem
A Focus for Analytical Chemistry in Europe

Evaluating the precision component of measurement uncertainty

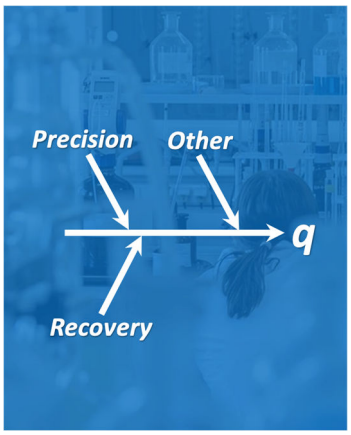
B. Magnusson

Eurachem on-line workshop
25-26 October 2022
Measurement uncertainty evaluation
based on in-house validation data

1

Eurachem
A Focus for Analytical Chemistry in Europe

Draft Eurachem Guide



2

Eurachem
A Focus for Analytical Chemistry in Europe

Measurement uncertainty components from in-house data in Eurachem draft guide

In-house overall precision

s

Recovery data

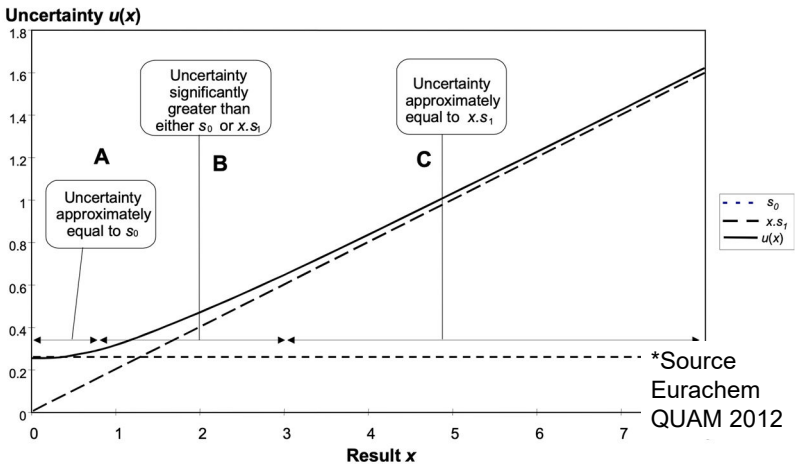
q_R

Eurachem - In-house validation data for MU 2022 3

3

Eurachem
A Focus for Analytical Chemistry in Europe

Uncertainty varies with concentration*



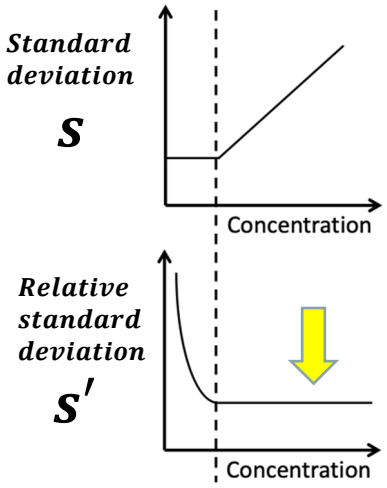
*Source Eurachem QUAM 2012

Eurachem - In-house validation data for MU 2022 4

4

Eurachem
A Focus for Analytical Chemistry in Europe

Precision varies in the same way



Eurachem - In-house validation data for MU 2022 5

5

Eurachem
A Focus for Analytical Chemistry in Europe

Evaluating the precision component at higher concentrations

We evaluate the relative standard deviation (RSD, CV%) Symbol used in the Eurachem draft Guide is

s'

Eurachem - In-house validation data for MU 2022 6

6

Eurachem
A Focus for Analytical Chemistry in Europe

Measurement precision

"The measurement precision is typically a **major** uncertainty component that can be easily quantified from experimental data."

We need **many** results to calculate a reliable standard deviation – e.g. the expanded uncertainty of the value of s is 28 % if n = 100

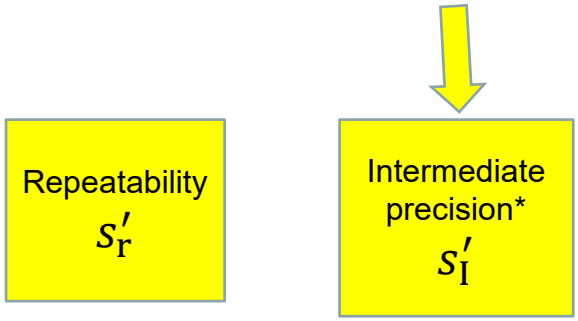
Note (as in ISO 5725-1) the expanded uncertainty of an estimated standard deviation s relative to its true value σ is $\approx 2/\sqrt{2n}$

Eurachem - In-house validation data for MU 2022 7

7

Eurachem
A Focus for Analytical Chemistry in Europe

Measurement precision in the laboratory



*Also called within-lab reproducibility

Eurachem - In-house validation data for MU 2022 8

8

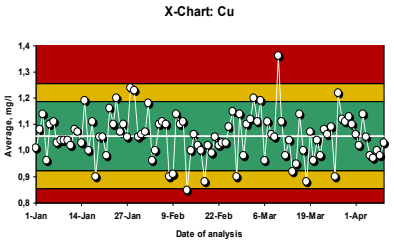
Eurachem
A Focus for Analytical Chemistry in Europe

Calculate intermediate precision s_I'

Control sample covering the whole analytical process

- Choose
  - QC sample in high concentration
  - control values from a long time
- Review the data for outliers*
- Calculate the

$$s_I'$$



*A pragmatic approach is to exclude data that are more than 4 standard deviations away from the central line and retain the rest (ISO 13530:2010)

Eurachem
A Focus for Analytical Chemistry in Europe

Measurement precision in the laboratory

Repeatability
s_r'

Intermediate precision*
s_I'

*Also called within-lab reproducibility

Eurachem
A Focus for Analytical Chemistry in Europe

Repeatability

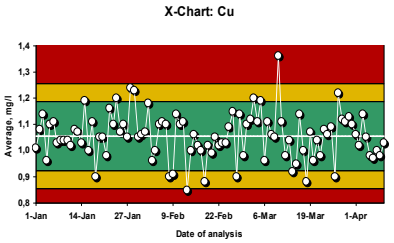
Test sample covering the whole analytical process

Approach A – when duplicates are in QC

- Use routine test sample in the higher concentration range - test results from duplicates over a longer time period
- Review the data for clear outliers
- Pool the data to get

$$s_r'$$

Advantage – you get s_r' for your test samples!



Eurachem - In-house validation data for MU 2022 11

11

Eurachem
A Focus for Analytical Chemistry in Europe

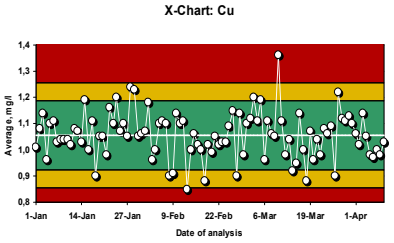
Repeatability

Test sample covering the whole analytical process

Approach B

- Measure several sample 10 times under repeatability conditions
- Pool the data to get

$$s_r'$$



Eurachem - In-house validation data for MU 2022 12

12

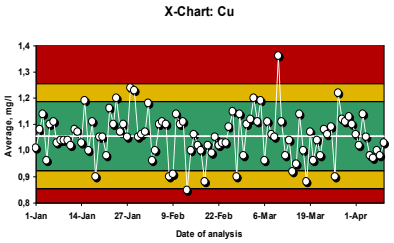
Eurachem
A Focus for Analytical Chemistry in Europe

Repeatability

Assessing the obtained repeatability standard deviation

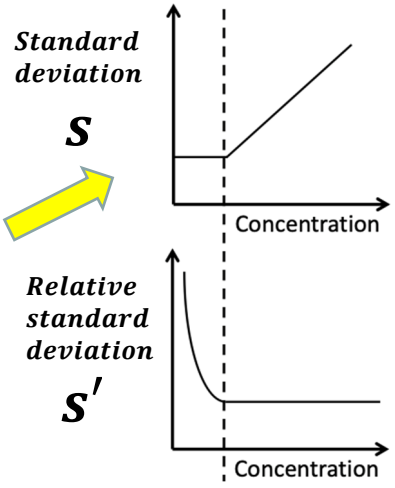
When implementing a standard method, the s'_r obtained can be compared with precision data given in the standard.

$$s'_{\mathrm{r}} \approx s'_{\mathrm{r\_method}}$$



Eurachem
A Focus for Analytical Chemistry in Europe

Now the low concentration range in the same way but calculate *s*



Eurachem
A Focus for Analytical Chemistry in Europe

Summary

For measurement uncertainty we need a reliable estimate of intermediate precision

s_I at low concentrations and

s_I' at high concentrations

In-house overall precision	Recovery data
s_I'	q_R'

Eurachem - In-house validation data for MU 2022 15

15

Eurachem
A Focus for Analytical Chemistry in Europe

THANKS FOR LISTENING

Now open for questions!

16