VARIATION OF THE MEASUREMENT UNCERTAINTY WITH MEASURAND LEVEL

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Top down evaluation of measurement uncertainty - Measurand level (often concentration) dependence

- Based on different types of precision and bias
- Often calculated from samples at different concentration levels
- Important to know the concentration dependence of the measurement uncertainty

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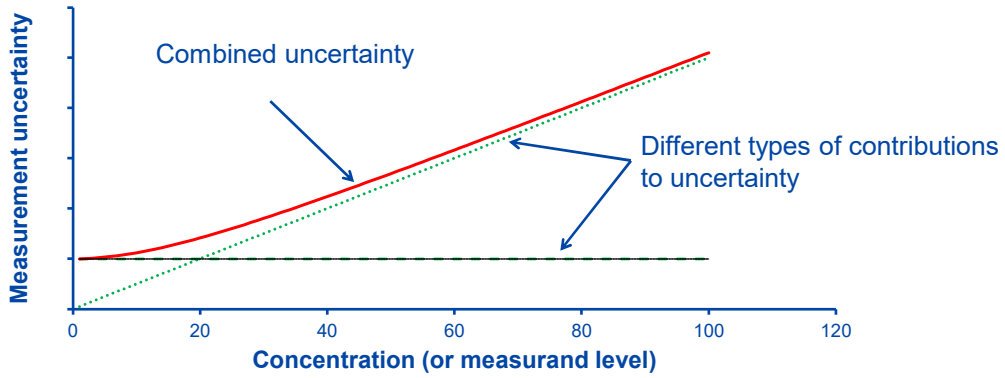
Typical dependence of concentration (measurand level) on measurement uncertainty for many instrumental techniques



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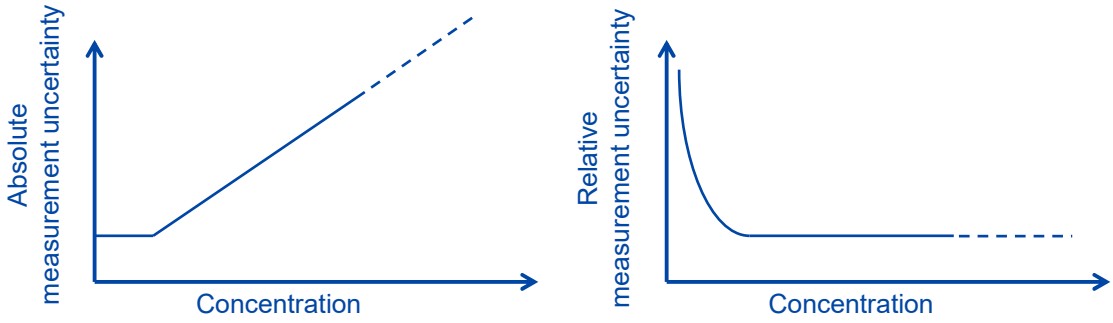
Typical dependence of concentration (measurand level) on measurement uncertainty for many instrumental techniques

Simplification:



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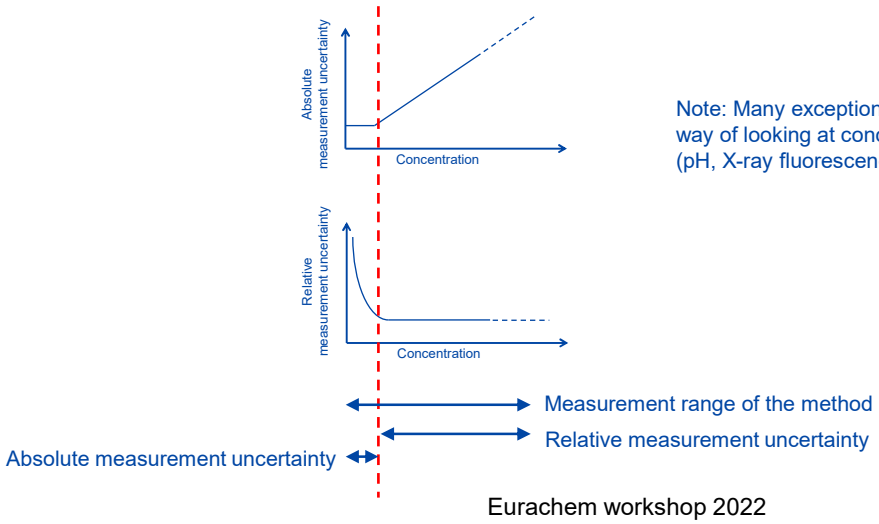
Typical dependence of concentration (measurand level) on measurement uncertainty for many instrumental techniques



Note: Many exceptions exist to this simplified way of looking at concentration dependence (pH, X-ray fluorescence, ……)

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To reality – What is the concentration dependence for your method?

To study this, ideally large amount of data is needed that are rarely available

Way of studying dependence of concentration (measurand level) on measurement uncertainty

Precision:

- ❑ Results for duplicates (repeatability)
- ❑ Performance data in standard methods (repeatability and reproducibility)
- ❑ Precision in proficiency testing schemes (reproducibility)

Bias:

- ❑ Data at many concentration levels rarely available

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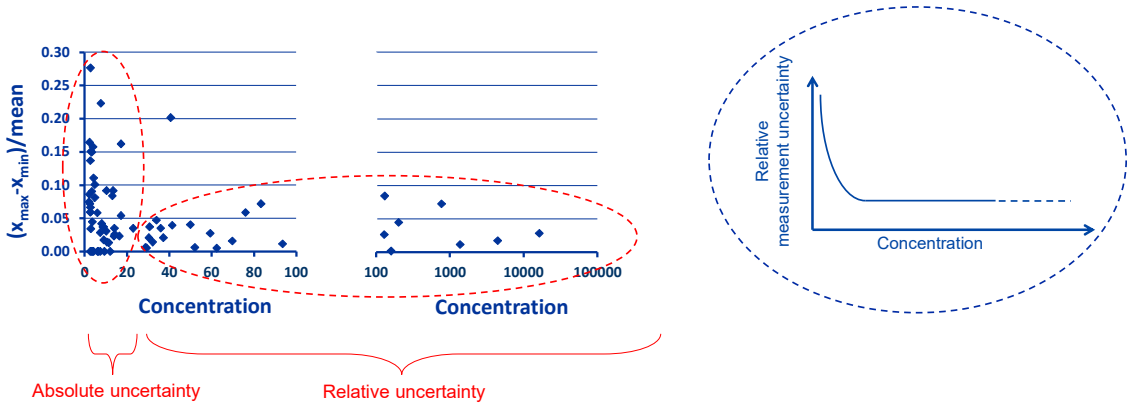
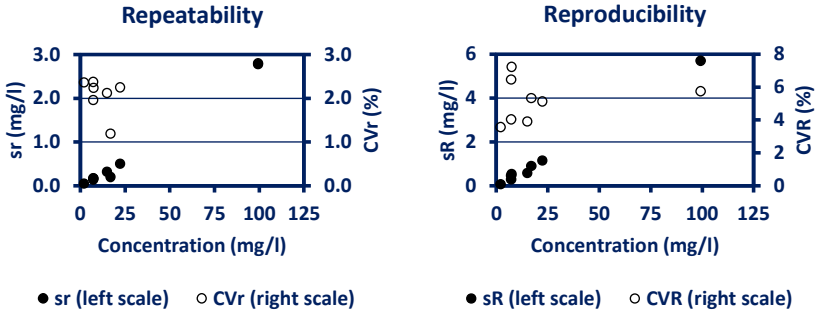
Way of studying dependence of concentration on measurement uncertainty
Results for duplicates (repeatability)



Determination of ammonium-nitrogen (EN ISO 11732). Data from Nordtest NT TR 537 (ed. 4, 2017).

Way of studying dependence of concentration on measurement uncertainty
Performance data in standard methods

- In many standard methods repeatability and reproducibility are given as absolute and relative standard deviation at different concentration levels.
- Examples



Way of studying dependence of concentration on measurement uncertainty

Precison in proficiency testing schemes (reproducibility)

From participation in proficiency test schemes covering different concentrations reproducibility expressed as absolute and relative standard deviation can give information of the concentration dependence.

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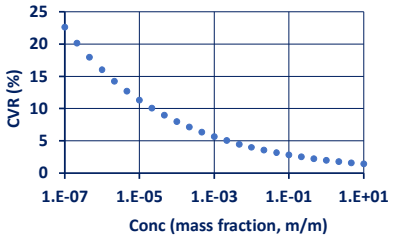
More on concentration dependence - Horwitz trumpet

For interlaboratory collaborative studies in food analysis:

$$s_R = 0.02 \times c^{0.85} \quad \text{or} \quad CV(\%) = 2 \times c^{-0.15}$$

where s_R is the reproducibility, $CV(\%)$ is the coefficient of variation in %, and c is concentration as mass fraction (m/m)



Note: This relationship is for large concentration ranges, and includes variation between different methods and instrumental techniques used at different concentration levels.

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Uncertainty expressed as coverage interval

When expressing uncertainty as a coverage interval and

- ❑ the relative uncertainty is approx. independent of the concentration
- ❑ the (combined) standard uncertainty is > approx. 15-20 %

it is necessary to consider asymmetry in the uncertainty coverage interval

The best way of handling this is under discussion.

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The end!

Thank you for listening

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