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Modelling uncertainty across the working range

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Outline

- Analytical range wideness
- Top-down uncertainty components
- Precision evaluation approaches
- Final remarks

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☐ Analytical range wideness

Measurement procedures can be designed to target:

- Narrow analytical ranges
 - Active substances in medicines
 - Seawater pH
 - Protein content in meat products
- Wide analytical ranges
 - Drinking water contaminants
 - Pesticide residues in foodstuffs

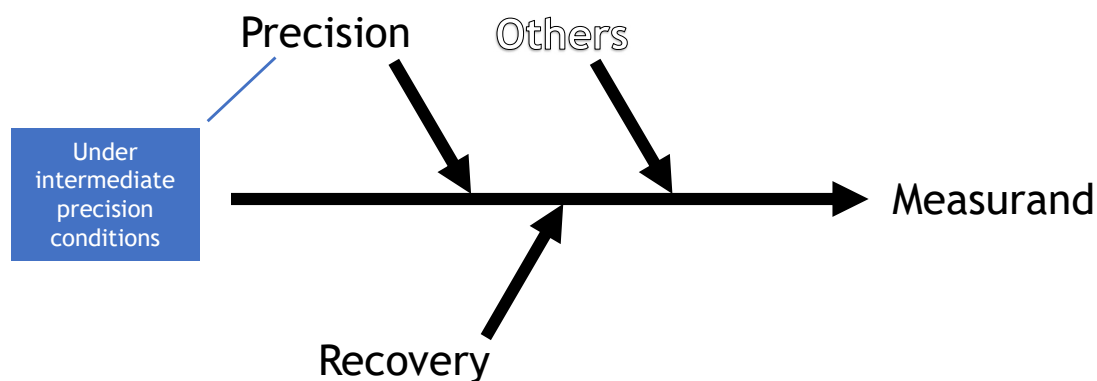
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☐ Top-down uncertainty components

Evaluation of the MU based on in-house method validation or test quality control



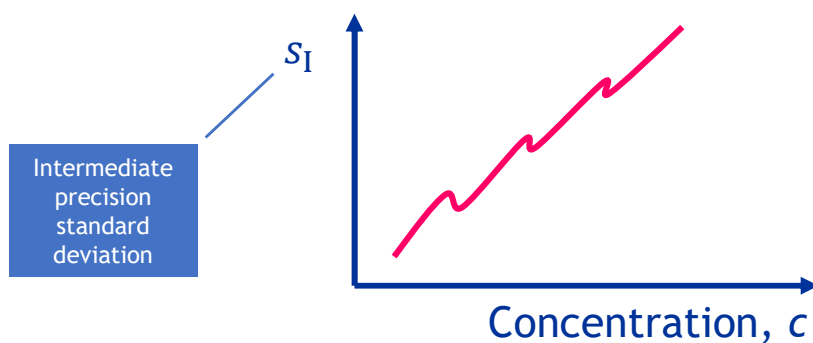
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Measurement precision

Measurement precision is known to vary in a wide concentration interval §



§ Term used in a general sense for any type of quantity

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Measurement recovery

If no chemical limits are achieved, such as:

- Reagents consumption
- Analyte precipitation ... (other than gravimetries)
- Deviation to regression model in instrumental methods

Then, analyte recovery is rather constant in the analytical range...

§ Term used in a general sense for any type of quantity

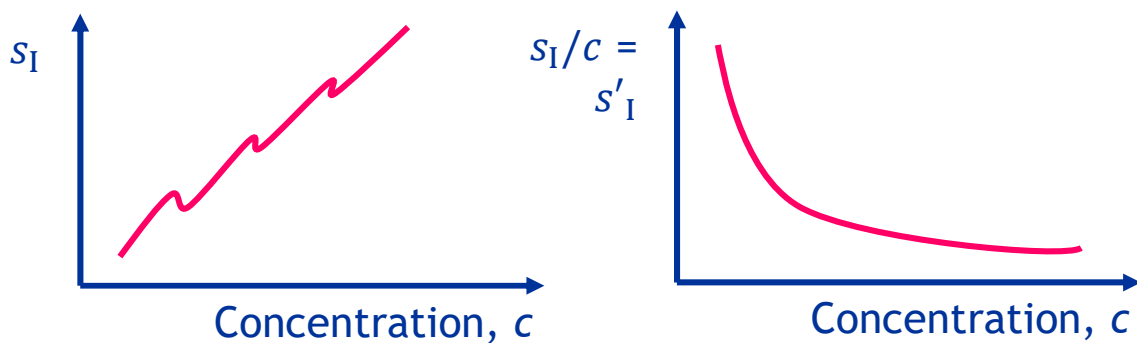
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Measurement precision (2)

Measurement precision is known to vary in a wide concentration interval §



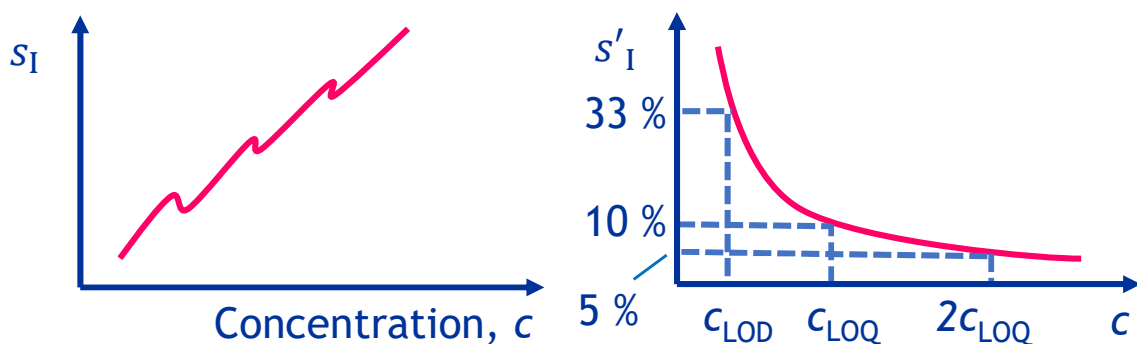
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Measurement precision (2)

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Measurement precision (2)

An accurate description of precision variation over the analytical interval would require performing many replicate analyses at various concentration levels...



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Measurement precision (2)

An accurate description of precision variation over the analytical interval would require performing many replicate analyses at various concentration levels...

Frequently, this effort is not necessary...

You just need to do what is necessary!



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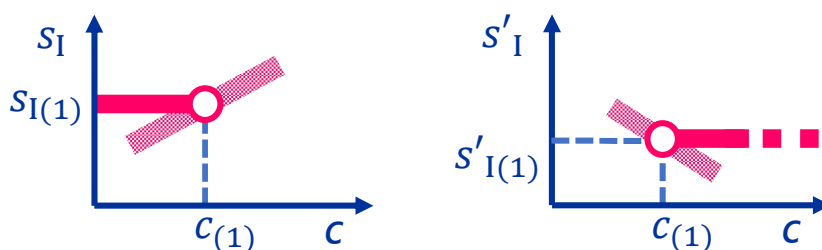
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© Precision evaluation approaches

Given the trends in measurement precision discussed, different approaches can be followed:

- (1) Worst-case extrapolation of precision estimated at one concentration level



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Given the trends in measurement precision discussed, different approaches can be followed:

- (1) Worst-case extrapolation of precision estimated at one concentration level

Example B1 of the Guide:

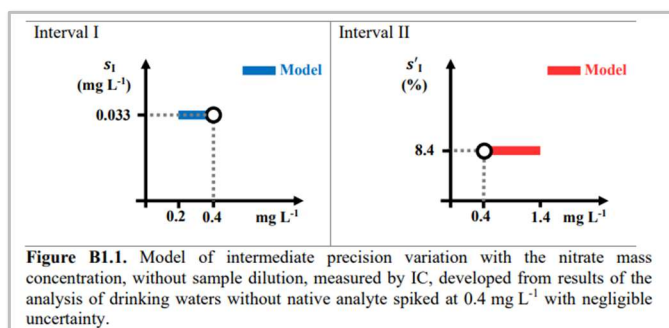


Figure B1.1. Model of intermediate precision variation with the nitrate mass concentration, without sample dilution, measured by IC, developed from results of the analysis of drinking waters without native analyte spiked at 0.4 mg L⁻¹ with negligible uncertainty.

Eurachem/CITAC Guide: Evaluation of measurement uncertainty from in-house precision and recovery data. First Edition, Eurachem, 2026.

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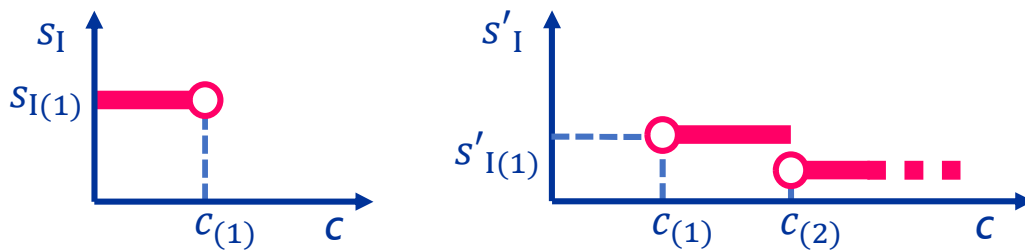
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☐ Precision evaluation approaches

Given the trends in measurement precision discussed, different approaches can be followed:

(2) Worst-case extrapolation of precision estimated at two concentration levels



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☐ Precision evaluation approaches

Given the trends in measurement precision discussed, different approaches can be followed:

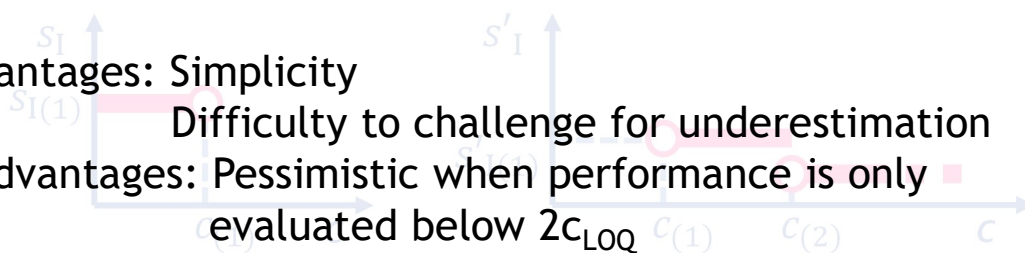
(2) Worst-case extrapolation of precision estimated at two concentration levels

Advantages: Simplicity

Difficulty to challenge for underestimation

Disadvantages: Pessimistic when performance is only

evaluated below $2c_{LOQ}$



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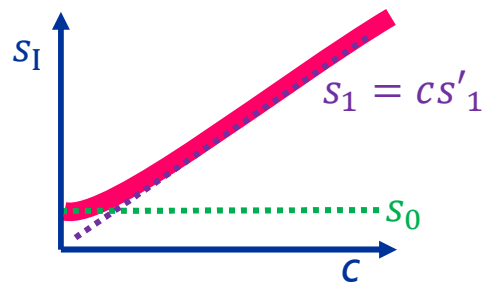
☐ Precision evaluation approaches

(...) (3) Some authors defend s_1 vs c can be described as a combination of a constant and a relative term:

$$s = \sqrt{s_0^2 + (c \cdot s'_1)^2}$$

s_0 - estimated close to c_{LOD}

s'_1 - estimated at high c



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☐ Precision evaluation approaches

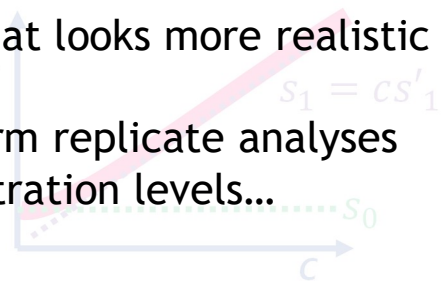
(...) (3) Some authors defend s_1 vs c can be described as a combination of a constant and a relative term:

Advantages: Continuous model that looks more realistic

Disadvantage: The need to perform replicate analyses at unusual concentration levels...

s_0 - estimated close to c

s'_1 - estimated at high c



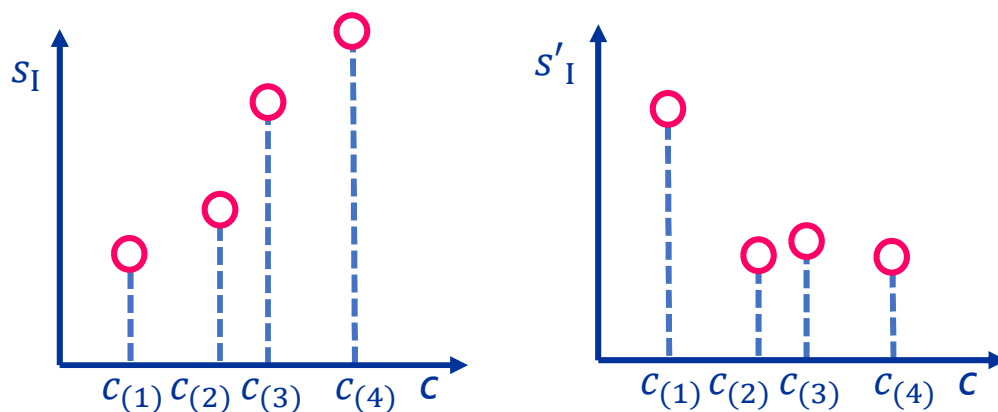
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Precision evaluation approaches

(...) (4) If s_I is estimated at various c , it can be attempted a regression line for s_I vs c or s'_I vs c :



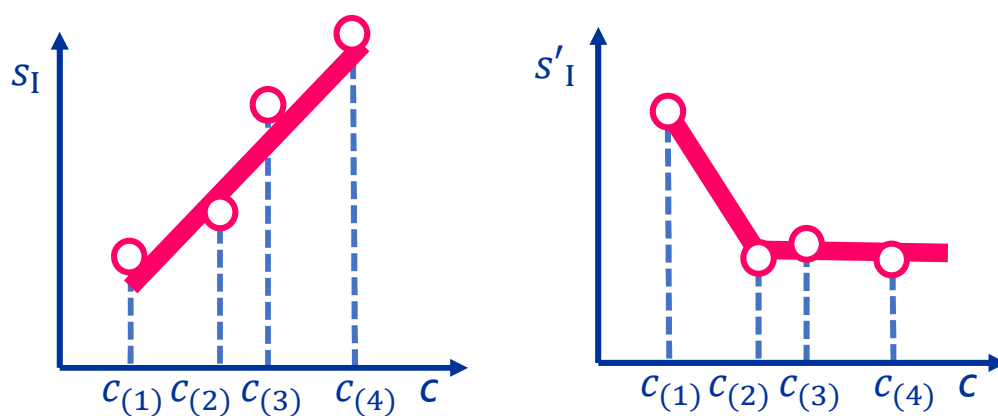
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Precision evaluation approaches

(...) (4) If s_I is estimated at various c , it can be attempted a regression line for s_I vs c or s'_I vs c :



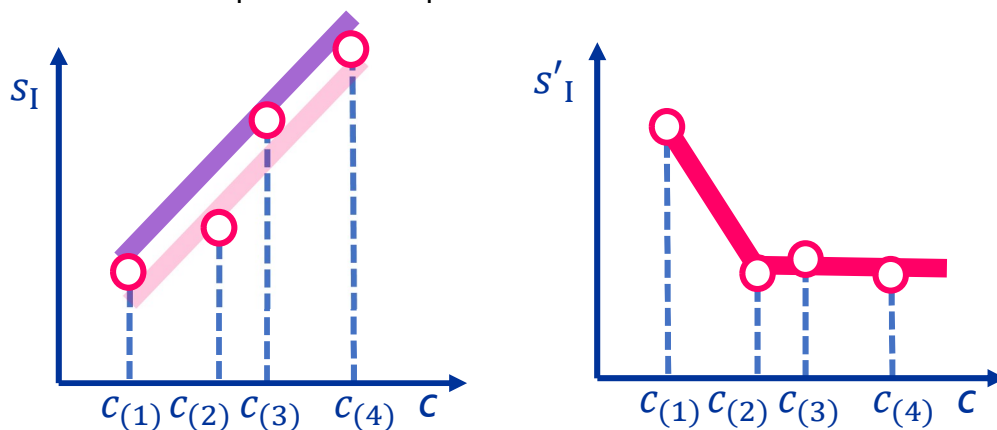
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Precision evaluation approaches

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Precision evaluation approaches

(...) (4) If s_I is estimated at various c , it can be attempted a regression line for s_I vs c or s'_I vs c :

Example B3 of the Guide:

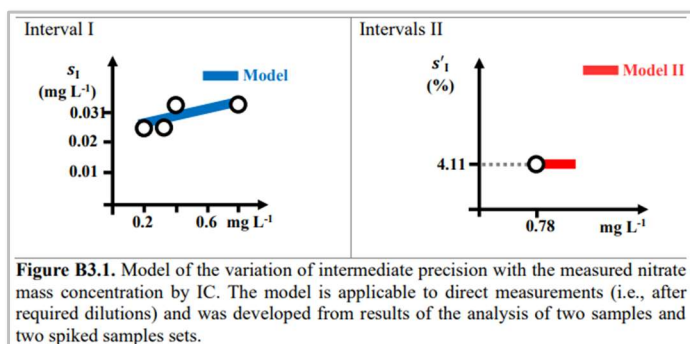


Figure B3.1. Model of the variation of intermediate precision with the measured nitrate mass concentration by IC. The model is applicable to direct measurements (i.e., after required dilutions) and was developed from results of the analysis of two samples and two spiked samples sets.

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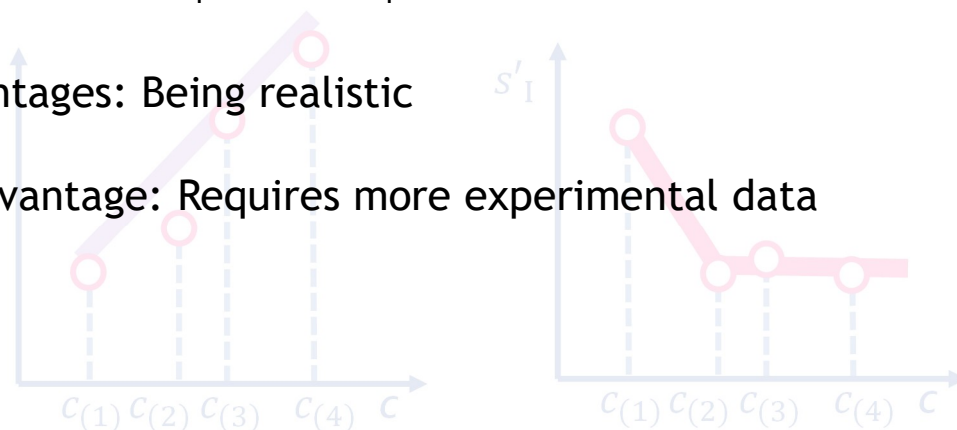
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☐ Precision evaluation approaches

(...) (4) If s_1 is estimated at various c , it can be attempted a regression line for s_1 vs c or s'_1 vs c :

Advantages: Being realistic

Disadvantage: Requires more experimental data



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☐ Precision evaluation approaches

Any approach can be applied if:

- Its limitations are understood and communicated
- Reported performance is fit for the intended use



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How to proceed when reporting the mean, \bar{x} , of replicate results

Number of replicates?

Time scale of replication?



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How to proceed when reporting the mean, \bar{x} , of replicate results

1st - Check the agreement between replicas adequately

When sample is analysed in p days and on each day n times:

$$s_I(\bar{x}(n, p)) = \sqrt{\frac{s_I^2}{p} + \frac{s_r^2(1-n)}{np}}$$

Intermediate precision standard deviation of the mean of $n \times p$ replicas

repeatability variance

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How to proceed when reporting the mean, \bar{x} , of replicate results

Example: mean of duplicates under repeatability conditions:

$$s_I(\bar{x}(n, p)) = \sqrt{\frac{s_I^2}{p} + \frac{s_r^2(1-n)}{np}} \Leftrightarrow$$

$$\Leftrightarrow s_I(\bar{x}(2, 1)) = \sqrt{s_I^2 + \frac{s_r^2(1-2)}{2}} = \sqrt{s_I^2 - \frac{s_r^2}{2}}$$

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How to proceed when the intermediate precision is estimated from the analysis of items more homogeneous than “real” samples:



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How to proceed when the intermediate precision is estimated from the analysis of items more homogeneous than “real” samples:

$$s_I \left(\bar{\bar{x}}_{(h)}(n, p) \right) = \sqrt{\frac{s_{r(h)}^2}{np} + \frac{s_I^2 - s_r^2}{p}}$$

Intermediate precision standard deviation of the mean of $n \times p$ replicas of the analysis of heterogeneous samples

repeatability variance for heterogeneous items

repeatability variance for homogenous items

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© Combined uncertainty

Measurement precision model should be combined with...

Components combined as absolute or relative standard uncertainties



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Final remark

Different approaches to modelling the variation of the measurement uncertainty can be applied...

Perhaps the best strategy is to use...
 the simplest ones that
 do not underestimate the MU and
 allow reporting a MU smaller than the target value
 (i.e. maximum admissible MU).

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Different approaches to modelling the variation of the measurement uncertainty can be applied...

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Thank you for
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