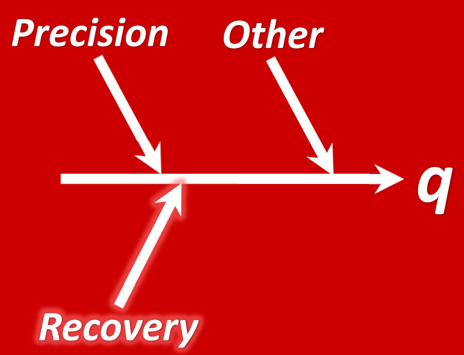
Evaluating the recovery component of measurement uncertainty



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Outline

- Introductory information
- Types of reference materials
- Calculation of mean recovery uncertainty
- Assessing mean recovery value
- Management of the variation of recovery with the sample matrix
- Uncertainty of results not corrected for recovery
- Final remarks

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Aim of recovery evaluation

To quantify the impact of between-days systematic effects on results.

Systematic effects can be constant:

- **In a relative way: *e.g.*, analyte losses and matrix effects**
- **In an absolute way: *e.g.*, analyte contamination and additive interferences – More relevant in low concentration ranges**

This distinction is not relevant in narrow concentration ranges

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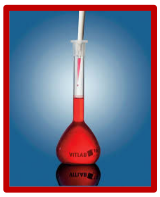
Reference materials

The assessment of systematic effects requires the analysis of samples with a reference value:

- **Certified reference material (CRM)**
- **Reference material from a proficiency test (PT)**
- **Reference material characterised by another method or lab (AL)**
- **Spiked sample without native analyte (SS)**
- **Spiked sample WITH native analyte (SWN)**



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Systematic effects uncertainty

The assessment of systematic effects is affected by:

- **Measurement precision**
- **Reference value uncertainty**
- **Sample matrix**

To reduce the impact of measurement precision, mean measured values are considered.

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Mean recovery

Particularly useful for systematic effects proportional to the analyte level, these can be quantified by the mean recovery, $\bar{R}$:

$$\bar{R} = \frac{\bar{q}}{Q}$$

$\bar{q}$ **– mean measured value**
Q **– reference value**

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Recovery types

Recovery: Usually associated with potential analyte loss from sample digestion and extraction.

Apparent recovery: Can be used when no analyte losses are expected.

D Burns et al, Use of the terms "recovery" and "apparent recovery" in analytical procedures, Pure Appl. Chem., 74 (2002) 2201–2205.

Mean recovery correction

After estimating $\bar{R}$, it is necessary to assess if $\bar{R}$ is fit for the intended use.
In some cases, the $\bar{R}$ must be equivalent to 100%:

$$\frac{|1-\bar{R}|}{u_{\bar{R}}} \leq 2$$

- yes → **Report original estimate, q**
- no → **Report corrected result, $q_c = q/\bar{R}$**

Mean recovery uncertainty

The uncertainty of the mean recovery is calculated depending on:

- **Types of reference materials: SWN or others (CRM, PT, etc.)**
- **Number of reference materials**
- **Relevance of sample matrix**

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Reference material except SWN

If one reference material is analysed in *m* different days (*j* = 1 to *n*):

$$\bar{R} = \frac{\sum q_j/m}{Q} = \frac{\bar{q}}{Q}$$

Mean measured value ($\bar{q}$)

Reference value (Q)

and:

$$u_{\bar{R}} = \bar{R}\sqrt{\left(\frac{s_{\mathrm{I}}(q_j)}{\bar{q}\sqrt{m}}\right)^2 + \left(\frac{u(Q)}{Q}\right)^2}$$

Intermediate precision standard deviation ($s_{\mathrm{I}}(q_j)$)

Standard uncertainty of *Q* ($u(Q)$)

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Reference material except SWN

If N ref. materials are analysed n_i times on different days (i = 1 to N):

$$\bar{R} = \frac{\sum \bar{R}_i}{N} = \frac{\sum \bar{q}_i / Q_i}{N} =$$

Mean measured value of the i^{th} reference material

Reference value of the i^{th} reference material

and:

$$u_{\bar{R}} = \sqrt{\sum_{i=1}^{N} \left\{ \left(\frac{\bar{q}_i}{Q_i} \right)^2 \left[\left(\frac{s_I(q_i)}{\bar{q}_i \sqrt{n_i}} \right)^2 + \left(\frac{u(Q_i)}{Q_i} \right)^2 \right] \right\} / N}$$

Intermediate precision standard deviation at q_i

If n_i < 10, $s_I(q_i)$ is estimated from precision models

Ref. mat. except SWN – Example

Determination of pyrene in water

Recovery from the analysis of spiked samples without native analyte, SS:

SS*i*	Q_i/ µg L-1	$u(Q_i)$/ µg L-1	$\bar{q}_i$/ µg L-1	$s_I(q_i)$/ µg L-1	n_i	$T_i = \left(\frac{\bar{q}_i}{Q_i}\right)^2 \left[\left(\frac{s_I(q_i)}{\bar{q}_i\sqrt{n_i}}\right)^2 + \left(\frac{u(Q_i)}{Q_i}\right)^2\right]$
SS1	1.5	0.041	1.460	0.0620 *	5	0.00105
SS2	1.5	0.041	1.446	0.0164	10	0.000706
SS3	1.5	0.041	1.456	0.000894 *	5	0.000711
SS4	1.5	0.041	1.458	0.0148 *	5	0.000725
* - precision models				$\sqrt{\sum T_i / 4}$		**0.0141**

R. Mateos et al., Impact of recovery correction or subjecting calibrators to sample preparation on measurement uncertainty: PAH determinations in waters, Talanta 207 (2020) 120274

Reference material except SWN

If, at least, a pair of the *N* estimated $\bar{R}_i$ are not compatible because:

$$|\bar{R}_{\mathrm{A}} - \bar{R}_{\mathrm{B}}| > 2\sqrt{u_{\bar{R}}^2(\bar{R}_{\mathrm{A}}) + u_{\bar{R}}^2(\bar{R}_{\mathrm{B}})}$$

The analytical scope can be divided into matrices with equivalent $\bar{R}$ or the u_{P} should be increased by adding a term:

Relative standard deviation of the mean recoveries

Interval I $[q_{\mathrm{LOQ}}, 2q_{\mathrm{LOQ}}]$: $u_{\mathrm{P}}\langle \mathrm{I} \rangle = \sqrt{s_{\mathrm{I}}^2\langle \mathrm{I} \rangle + \left(s'(\bar{R}_i) \cdot 2q_{\mathrm{LOQ}}\right)^2}$

Interval II $[2q_{\mathrm{LOQ}}, q_{\mathrm{Max}}]$: $u'_{\mathrm{P}}\langle \mathrm{II} \rangle = \sqrt{s'^2_{\mathrm{I}}\langle \mathrm{II} \rangle + s'^2(\bar{R}_i)}$

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Ref. mat. except SWN – Example

Compatibility of estimated mean recoveries
Determination of pyrene in water: Recovery from the analysis of SS

			$\lvert\bar{R}_o - \bar{R}_p\rvert / \sqrt{u_{\bar{R}_o}^2 + u_{\bar{R}_p}^2}$		
			$\bar{R}_i; u(\bar{R}_i)$		
SSi	$\bar{R}_i$	$u(\bar{R}_i)$	**SS2**	**SS3**	**SS4**
SS1	97.3%	3.24%	0.223	0.064	0.032
SS2	96.4%	2.66%		0.177	0.211
SS3	97.1%	2.67%			0.035
SS4	97.2%	2.69%			
Compatible if $\lvert\bar{R}_o - \bar{R}_p\rvert / \sqrt{u_{\bar{R}_o}^2 + u_{\bar{R}_p}^2} \leq 2$					

R. Mateos et al., Impact of recovery correction or subjecting calibrators to sample preparation on measurement uncertainty: PAH determinations in waters, Talanta 207 (2020) 120274

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Reference material SWN

One spiked sample with native analyte is analysed where the pair sample before and after spiking is analysed on the same day:

Mean of spiked sample results from n analysis

Mean of native analyte results from m analysis

Spiked value

$$\bar{R} = \frac{\bar{q} - \bar{q}_0}{q_+}$$

and:

Repeatability standard deviations

$$u_{\bar{R}} = \bar{R}\sqrt{\left(\frac{\frac{s_r^2(q_j)}{n} + \frac{s_r^2(q_{0j})}{m}}{(\bar{q} - \bar{q}_0)^2}\right) + \left(\frac{u(q_+)}{q_+}\right)^2}$$

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Reference material SWN

If *N* samples with native analyte are analysed, where the pair $\bar{q}_j$ and $\bar{q}_{0j}$ are determined under repeatability conditions:

$$\bar{R} = \frac{\sum_{i=1}^{N} (\bar{q}_i - \bar{q}_{0i})/q_{+i}}{N}$$

and:

$$u_{\bar{R}} = \sqrt{\sum_{i=1}^{N}\left\{\left(\frac{\bar{q}_i - \bar{q}_{0i}}{q_{+i}}\right)^2\left[\left(\frac{\frac{s_r^2(q_i)}{n_i} + \frac{s_r^2(q_{0i})}{m_i}}{(\bar{q}_i - \bar{q}_{0i})^2}\right) + \left(\frac{u(q_{+i})}{q_{+i}}\right)^2\right]\right\}\Big/ N}$$

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Reference material SWN

If N samples with native analyte are analysed, where the pair $\bar{q}_j$ and $\bar{q}_{0j}$ are determined under repeatability conditions:

$$\bar{R} = \frac{\sum_{i=1}^{N} (\bar{q}_i - \bar{q}_{0i})/q_{+i}}{N}$$

(…)

It can be tested if estimated $\bar{R}_i$ are compatible to decide on the need to add the standard deviation of mean recoveries, $s'(\bar{R}_i)$.

Pooling various recoveries

The recoveries estimated from all types of reference materials can be compared and pooled:

$$\bar{\bar{R}} = \frac{\sum_{k=1}^{M} \bar{R}_k}{M}$$

and:

$$u_{\bar{\bar{R}}} = \sqrt{\frac{\sum_{k=1}^{M} (n_k - 1) u^2(\bar{R}_k)}{\sum_{k=1}^{M} (n_k - 1)}}$$

It must be assessed if results must be corrected for the mean recovery

Not correcting for recovery

If $\bar{\bar{R}}$ does not meet the requirement (e.g., $\bar{\bar{R}}$ not equivalent to 1) and it is decided not to correct results for recovery, an additional uncertainty component must be considered:

$$U_{\mathrm{bc}} = U + q\left|\left(\bar{\bar{R}} - 1\right)/\bar{\bar{R}}\right|$$

$$u_{\bar{\bar{R}}} = \bar{\bar{R}}\sqrt{\frac{\sum_{k=1}^{M}(\bar{R}_k - 1)^2}{M} + \frac{\sum_{k=1}^{M}(u(Q_k)/Q_k)^2}{M}}$$

1. IUPAC/ISO/AOACInt, Harmonised guidelines for the use of recovery information in analytical measurement (Technical Report), 1998.
2. B. Magnusson et al., Handbook for calculation of measurement uncertainty in environmental laboratories (NT TR 537 – Edition 4), 2017.

Not correcting for recovery

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Not equivalent to recovery correction!

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2. B. Magnusson et al., Handbook for calculation of measurement uncertainty in environmental laboratories (NT TR 537 – Edition 4), 2017.

Final remarks

- Formulas are only complex before you have applied them for the first time.
- Software can easily facilitate the use of formulas in routine analysis.
- Most customers will not value accurate uncertainty evaluations but, assessors and analysts value a better management of MU

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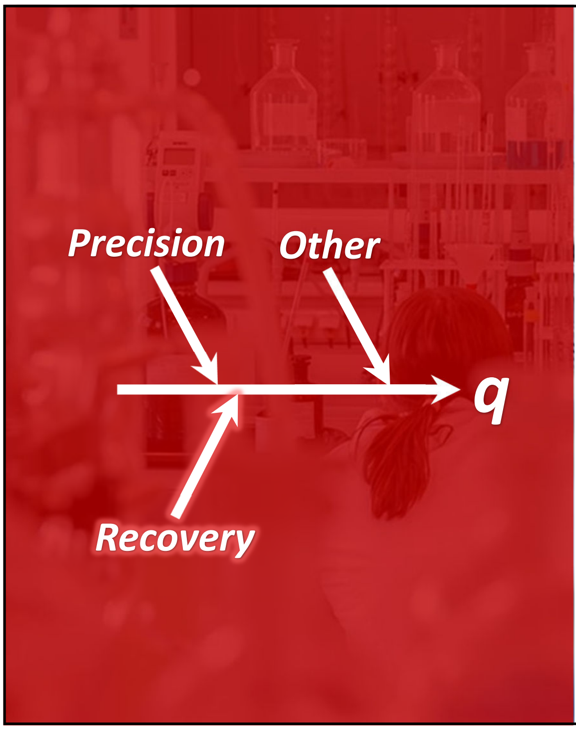

Thanks for your attention

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