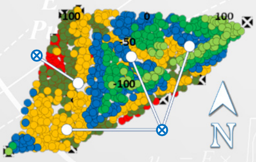
Critical Issues of the Accreditation Standards
Nicosia, 21-22 February 2019

Uncertainty from sampling



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21 Feb. 2019

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Overview

1. Sampling accreditation
2. Analysis of the collected sample
3. Analysis of a large item
4. Exercise

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1. Sampling accreditation

It can be accredited two types of sampling work:

Task 1: Collection and transport of a sample to the laboratory for analysis;

Task 2: Sampling a large item (e.g. large river area or food lot) in order to produce an adequate estimate of a parameter of the large item. Includes the activities of Task 1.

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1. Sampling accreditation

It can be accredited two types of sampling work:

Task 1: Measurand (quantity intended to be measured): The quantity value in the sample (e.g. nitrite concentration in the water sample);

Task 2: Measurand: The mean quantity value in the large item (e.g. the nitrite concentration in river area *X*, at 1 m depth, day *Y* and time *Z*.

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2. Analysis of the collected sample

Measurement uncertainty model ("top-down" approach):

Uncertainty components:

Sub-sampling(1)	Intermediate precision(2)	Trueness(3)

(1) Heterogeneity of the collected sample;

(2) Measurement intermediate precision ("between-days" precision);

(3) Component for systematic effects estimated from the analysis of items with reference value.

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2. Analysis of the collected sample

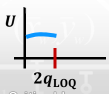
The analytical interval (known as "analytical range") is divided in two intervals:

Interval I: $[q_{\mathrm{LOD}},\ 2q_{\mathrm{LOQ}}[$ ➔ Combination of absolute uncertainty components;

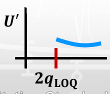
Interval II: $[2q_{\mathrm{LOQ}},\ q_{\mathrm{Max}}[$ ➔ Combination of relative uncertainty components.

where q_{LOD} is the Limit of Detection, q_{LOQ} is the Limit of Quantification and q_{Max} the maximum value studied during procedure validation. Some laboratories prefer to start the analytical internal at the q_{LOQ}.

Interval I



Interval II



$U' = U/q$

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2. Analysis of the collected sample

Interval I ($[q_{\mathrm{LOD}}, 2q_{\mathrm{LOQ}}[$):

$$U(q) = 2\sqrt{s^2_{\mathrm{r(h)}}\langle \mathrm{I}\rangle + s^2_{\mathrm{I}}\langle \mathrm{I}\rangle + (qu'_{\mathrm{T}})^2}$$

$s_{\mathrm{r(h)}}\langle \mathrm{I}\rangle$ - repeatability standard deviation of the analysis of heterogeneous samples with q within Interval I;

$s_{\mathrm{I}}\langle \mathrm{I}\rangle$ - intermediate precision standard deviation of the analysis of homogeneous samples with q within Interval I;

u'_{T} - trueness relative standard uncertainty estimated for Interval I and II;

$U(q)$ - expanded uncertainty of estimated quantity, q, for a confidence level of approximately 95 %.

2. Analysis of the collected sample

Interval I ($[q_{\mathrm{LOD}}, 2q_{\mathrm{LOQ}}[$):

$$U(q) = 2\sqrt{s^2_{\mathrm{r(h)}}\langle \mathrm{I}\rangle + s^2_{\mathrm{I}}\langle \mathrm{I}\rangle + (qu'_{\mathrm{T}})^2}$$

u'_{T} - trueness relative standard uncertainty estimated for Interval I and II:

$$u'_{\mathrm{T}} = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\}\Big/(N\bar{R})}$$

R_i – Recovery of test i (i = 1 to N);

$s'(R_i)$ – relative standard deviation of R_i;

$u'(Q_i)$ – relative standard uncertainty of the reference value, Q_i;

$\bar{R}$ – mean recovery ($\bar{R} = \sum R_i/N$).

where if:

$\frac{|1-\bar{R}|}{u_{\mathrm{T}}}$

- > 2 ➔ If allowed, correct recovery ($q = q_{\mathrm{initial}}/\bar{R}$);
- ≤ 2 ➔ Do not correct recovery.

2. Analysis of the collected sample

Interval I ($[q_{\mathrm{LOD}}, 2q_{\mathrm{LOQ}}[$):

$$U(q) = 2\sqrt{s^2_{\mathrm{r(h)}}\langle \mathrm{I}\rangle + s^2_{\mathrm{I}}\langle \mathrm{I}\rangle + (qu'_{\mathrm{T}})^2} \qquad u'_{\mathrm{T}} = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\}\Big/(N\bar{R})}$$

Example: Determination of total chromium in marine sediments:
$q_{\mathrm{LOQ}} = 7.5\ \mathrm{mg\ kg^{-1}}$

i) Analysis of sediments duplicates:

Date	x_1	x_2	Mean, m	Interval I or II	Interval I $\lvert x_1-x_2\rvert$ mg kg^{-1}	Interval II $\lvert x_1-x_2\rvert/m$
1	53.63	50.63	52.13	Interv. II	-	5.75%
2	40.80	40.29	40.545	Interv. II	-	1.26%
3	36.54	37.20	36.87	Interv. II	-	1.79%
4	13.54	14.14	13.84	Interv. I	0.6	-
5	21.97	21.08	21.525	Interv. II	-	4.13%
6	57.00	55.16	56.08	Interv. II	-	3.28%
7	33.62	34.14	33.88	Interv. II	-	1.53%
8	5.56	4.73	5.145	Interv. I	0.83	-
9	4.19	4.03	4.11	Interv. I	0.16	-
10	8.92	8.11	8.515	Interv. I	0.81	-
11	21.37	22.19	21.78	Interv. II	-	3.76%
(...)						
52	15.51	16.79	16.15	Interv. II	-	7.93%
53	88.67	93.27	90.97	Interv. II	-	5.06%
54	133.82	126.63	130.225	Interv. II	-	5.52%
55	9.41	9.74	9.575	Interv. I	0.33	-
				Mean	0.391	2.91%
				n	24	31
				$s_{\mathrm{r(h)}}\langle \mathrm{I}\rangle$	0.346	*
				$s_{\mathrm{r(h)}}\langle \mathrm{II}\rangle$		2.58% *

* - Mean/1.128

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2. Analysis of the collected sample

Interval I ($[q_{LOD}, 2q_{LOQ}[$):

$$U(q) = 2\sqrt{s^2_{r(h)}\langle I\rangle + s^2_I\langle I\rangle + (qu'_T)^2} \quad u'_T = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\}/(N\bar{R})}$$

Example: Determination of t[illegible]

$q_{LOQ} = 7.5$ mg kg^{-1}

i) Analysis of sediments duplicates:

Date	x_1	x_2	Mean, *m*	Interval I or II	Interval I $\lvert x_1-x_2\rvert$ mg kg^{-1}	Interval II $\lvert x_1-x_2\rvert/m$
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[illegible]	[illegible]	[illegible]	16.15	Interv. II	-	7.93%
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55	9.41	9.74	9.575	Interv. I	0.33	-
				Mean	0.391	2.91%
				n	24	31
				$s_{r(h)}$<I>	0.346	
				$s_{r(h)}$<II>		2.58% *

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$s_{r(h)} = 0.346$ mg kg^{-1}

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2. Analysis of the collected sample

Interval I ($[q_{LOD}, 2q_{LOQ}[$):

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Example: Determination of total chromium in marine sediments:

$q_{LOQ} = 7.5$ mg kg^{-1}

ii) Analysis of an homogeneous sediment in different days:

	Replicate results in Interval I			Replicate results in Interval II		
	Sample G	Sample H	Sample I	Sample J	Sample K	Sample L
				46.9		
				46.01		
				43.93		
				44.91		
				(...)		
				48.1		
				49.74		
				46.74		
Mean	-	-	-	47.17	-	-
SD	-	-	-	3.56	-	-
n	-	-	-	29	-	-
SD/Mean	-	-	-	7.54%	-	-

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2. Analysis of the collected sample

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				(...)		
				48.1		
				49.74		
				46.74		
[illegible]	[illegible]	[illegible]	-	47.17	-	-
[illegible]	[illegible]	[illegible]	-	3.56	-	-
n	-	-	-	29	-	-
SD/Mean	-	-	-	7.54%	-	-

$s_I = 2q_{LOQ}s'_I\langle II\rangle$
$= 2 \cdot 7.5 \cdot 0.0754$
$= 1.13$ mg kg^{-1}

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2. Analysis of the collected sample

Interval I ($[q_{\mathrm{LOD}}, 2q_{\mathrm{LOQ}}[$):

$$U(q) = 2\sqrt{s^2_{\mathrm{r(h)}}\langle\mathrm{I}\rangle + s^2_{\mathrm{I}}\langle\mathrm{I}\rangle + (qu'_{\mathrm{T}})^2} \qquad u'_{\mathrm{T}} = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\}\Big/(N\bar{R})}$$

Example: Determination of total chromium in marine sediments:

$q_{\mathrm{LOQ}} = 7.5$ mg kg^{-1}

iii) Analysis of samples from proficiency tests:

	Reference value		Estimated value, qi			
Proficiency test scheme	Q_i	$u(Q_i)$	Rep. 1 (Day a)	R_i	$u'(Q_i)$	$Ri^2[s'(R_i)^2+u(Q_i)^2]$
Round 1	26.816	1.206	37	138.0%	0.04497	2.3%
Round 2	75.098	3.484	91	121.2%	0.04639	1.8%
Round 3	75.334	3.931	92	122.1%	0.05218	1.9%
Round 4	313.37	7.445	367	117.1%	0.02376	1.4%
Round 5	27.199	1.935	32	117.7%	0.07114	2.1%
(...)						
Round 37	82.24	2.811	78	94.8%	0.03418	1.0%
Round 38	50.1	1.423	52.6	105.0%	0.0284	1.2%
Round 39	79.14	2.987	86.37	109.1%	0.03774	1.3%
Round 40	149	5.157	172	115.4%	0.03461	1.5%
			Mean	110.1%	u_{T}	1.885%
			SD	10.9%		
			$s'(R_i)$	9.937%		

|1-1.101|/(0.01885) = 5.333 → Recovery correction required

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2. Analysis of the collected sample

Interval I ($[q_{\mathrm{LOD}}, 2q_{\mathrm{LOQ}}[$):

$$U(q) = 2\sqrt{s^2_{\mathrm{r(h)}}\langle\mathrm{I}\rangle + s^2_{\mathrm{I}}\langle\mathrm{I}\rangle + (qu'_{\mathrm{T}})^2} \qquad u'_{\mathrm{T}} = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\}\Big/(N\bar{R})}$$

Example: Determination of total chromium in marine sediments:

$q_{\mathrm{LOQ}} = 7.5$ mg kg^{-1}

iii) Analysis of samples from proficiency tests:

$u'_{\mathrm{T}} = 0.01885/1.101$

Recovery correction is required (*1/1.101)

	Reference value		Estimated value, qi			
Proficiency test scheme	Q_i	$u(Q_i)$	Rep. 1 (Day a)	R_i	$u'(Q_i)$	$Ri^2[s'(R_i)^2+u(Q_i)^2]$
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2. Analysis of the collected sample

Interval I ($[q_{\mathrm{LOD}}, 2q_{\mathrm{LOQ}}[$):

$$U(q) = 2\sqrt{s^2_{\mathrm{r(h)}}\langle\mathrm{I}\rangle + s^2_{\mathrm{I}}\langle\mathrm{I}\rangle + (qu'_{\mathrm{T}})^2} \qquad u'_{\mathrm{T}} = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\}\Big/(N\bar{R})}$$

Example: Determination of total chromium in marine sediments:

Sample preservation quality control:

In order to prove that observed recovery is applicable to the analysis of samples collected from the river, field recovery tests are required (1).

The test quality control should also include the duplicate collection of samples and field blanks (2).

(1) – It can be spiked a sediment in the laboratory that travels from lab to field and back to the lab (it is difficult to measure a mass of sediment in the field);

(2) – Blank solution that travels from lab to field and back to the lab.

$s'(R_i)$ 9.937%

|1-1.101|/(0.01885) = 5.333 → Recovery correction required

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2. Analysis of the collected sample

Interval I ($[q_{\mathrm{LOD}}, 2q_{\mathrm{LOQ}}[$):

$$U(q) = 2\sqrt{s^2_{\mathrm{r(h)}}\langle \mathrm{I}\rangle + s^2_{\mathrm{I}}\langle \mathrm{I}\rangle + (qu'_{\mathrm{T}})^2} \quad \Bigg\| \quad u'_{\mathrm{T}} = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\} \Big/ (N\bar{R})}$$

Example: Determination of total chromium in marine sediments:
$q_{\mathrm{LOQ}} = 7.5\ \mathrm{mg\ kg^{-1}}$

iv) Uncertainty components combination (units mg kg^{-1}):

$$q = \frac{q_{\mathrm{initial}}}{1.101}$$

$$U(q) = 2\sqrt{0.346^2 + 1.13^2 + \left(q\frac{0.01885}{1.101}\right)^2}$$

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2. Analysis of the collected sample

Interval II ($[2q_{\mathrm{LOQ}}, q_{\mathrm{Max}}[$):

$$U'(q) = 2\sqrt{s'^2_{\mathrm{r(h)}}\langle \mathrm{II}\rangle + s'^2_{\mathrm{I}}\langle \mathrm{II}\rangle + u'^2_{\mathrm{T}}} \quad \Bigg\| \quad u'_{\mathrm{T}} = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\} \Big/ (\bar{R}N)}$$

$s'_{\mathrm{r(h)}}\langle \mathrm{II}\rangle$ - repeatability relative standard deviation of the analysis of heterogeneous samples with q within Interval II;

$s'_{\mathrm{I}}\langle \mathrm{II}\rangle$ - intermediate precision relative standard deviation of the analysis of homogeneous samples with q within Interval II;

u'_{T} - trueness relative standard uncertainty estimated for Interval I and II;

$U'(q)$ - relative expanded uncertainty of estimated quantity, q, for a confidence level of approximately 95 %.

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2. Analysis of the collected sample

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Example: Determination of total chromium in marine sediments:
$q_{\mathrm{LOQ}} = 7.5\ \mathrm{mg\ kg^{-1}}$

i) Analysis of sediments duplicates:

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				Mean	0.391	2.91%
				n	24	31
				$s_{\mathrm{r(h)}}$⟨I⟩	0.346	
				$s_{\mathrm{r(h)}}$⟨II⟩		2.58%

* - Mean/1.128

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2. Analysis of the collected sample

Interval II ([$2q_{\mathrm{LOQ}}$, q_{Max}[ ):

$$U'(q) = 2\sqrt{s'^2_{\mathrm{r(h)}}\langle \mathrm{II}\rangle + s'^2_{\mathrm{I}}\langle \mathrm{II}\rangle + u'^2_{\mathrm{T}}}$$

$$u'_{\mathrm{T}} = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\}/(\bar{R}N)}$$

Example: Determination of to[tal chromium in marine sediments:]

$q_{\mathrm{LOQ}} = 7.5$ mg kg^{-1}

i) Analysis of sediments duplicates:

Date	x_1	x_2	Mean, *m*	Interval I or II	Interval I $\|x_1-x_2\|$ mg kg^{-1}	Interval II $\|x_1-x_2\|/m$
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				Mean	0.391	2.91%
				n	24	31
				$s_{\mathrm{r(h)}}$<I>	0.346*	
				$s_{\mathrm{r(h)}}$<II>		2.58%*

* - Mean/1.128

$s'_{\mathrm{r(h)}} = 2.53$ %

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2. Analysis of the collected sample

Interval II ([$2q_{\mathrm{LOQ}}$, q_{Max}[ ):

$$U'(q) = 2\sqrt{s'^2_{\mathrm{r(h)}}\langle \mathrm{II}\rangle + s'^2_{\mathrm{I}}\langle \mathrm{II}\rangle + u'^2_{\mathrm{T}}}$$

$$u'_{\mathrm{T}} = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\}/(\bar{R}N)}$$

Example: Determination of tota[l chromium in marine sediments:]

$q_{\mathrm{LOQ}} = 7.5$ mg kg^{-1}

ii) Analysis of an homogeneous sediment in different days:

	Replicate results in Interval I			Replicate results in Interval II		
	Sample G	Sample H	Sample I	Sample J	Sample K	Sample L
				46.9		
				46.01		
				43.93		
				44.91		
				(...)		
				48.1		
				49.74		
				46.74		
Mean	-	-	-	47.17	-	-
SD	-	-	-	3.56	-	-
n	-	-	-	29	-	-
SD/Mean	-	-	-	7.54%	-	-

$s'_{\mathrm{I}} = 7.54$ %

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2. Analysis of the collected sample

Interval II ([$2q_{\mathrm{LOQ}}$, q_{Max}[ ):

$$U'(q) = 2\sqrt{s'^2_{\mathrm{r(h)}}\langle \mathrm{II}\rangle + s'^2_{\mathrm{I}}\langle \mathrm{II}\rangle + u'^2_{\mathrm{T}}}$$

$$u'_{\mathrm{T}} = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\}/(\bar{R}N)}$$

Example: Determination of total chromium in marine sediments:

$q_{\mathrm{LOQ}} = 7.5$ mg kg^{-1}

iii) Analysis of samples from proficiency tests:

$u'_{\mathrm{T}} = 0.01885/1.101$

Assessed previously!

Recovery correction is required (*1/1.101)

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2. Analysis of the collected sample

Interval II ($[2q_{\mathrm{LOQ}}, q_{\mathrm{Max}}[$):

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iv) Uncertainty components combination:

$$q = \frac{q_{\mathrm{initial}}}{1.101}$$

$$U(q) = 2q\sqrt{0.0253^2 + 0.0754^2 + \left(\frac{0.01885}{1.101}\right)^2} = q0.16$$

3. Analysis of a large item

Measurement uncertainty model ("top-down" approach):

Uncertainty components:

Sampling[(1)]	Intermediate precision[(2)]	Trueness[(3)]

(1) Uncertainty of heterogeneous item sampling;

(2) Measurement intermediate precision ("between-days" precision);

(3) Component for systematic effects estimated from the analysis of items with reference value.

3. Analysis of a large item

The characterisation of a large item requires the assessment of their heterogeneity from the analysis of *m* samples. For simplicity, it can be assumed the normal distribution of the studied quantity.

3. Analysis of a large item

Interval I ($[q_{LOD}, 2q_{LOQ}[$):

$$U(q) = 2\sqrt{\frac{s^2}{m} + s_{\mathrm{I}}^2\langle \mathrm{I}\rangle + (\bar{q}u'_{\mathrm{T}})^2} \qquad u'_{\mathrm{T}} = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\}\Big/(\bar{R}N)}$$

where s is the standard deviation of measured values of m samples analysed under repeatability conditions (small overestimation of repeatability).

Interval II ($[2q_{LOQ}, q_{Max}[$):

$$U(q) = 2q\sqrt{\frac{s'^2}{m} + s'^2_{\mathrm{I}}\langle \mathrm{II}\rangle + u'^2_{\mathrm{T}}}$$

For Interval I or II, the sampling standard, s_{S}, or relative standard, s'_{S}, uncertainty is estimated by $s_{\mathrm{S}} = (s^2/m - s_{\mathrm{r}}^2\langle \mathrm{I}\rangle/m)^{1/2}$ or $s'_{\mathrm{S}} = (s'^2/m - s'^2_{\mathrm{r}}\langle \mathrm{II}\rangle/m)^{1/2}$, respectively; where $s_{\mathrm{r}}\langle \mathrm{I}\rangle$ and $s'_{\mathrm{r}}\langle \mathrm{II}\rangle$ are the standard deviation or relative standard deviation of measurements repeatability for Internal I and II, respectively.

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3. Analysis of a large item

(…)

Interval II ($[2q_{LOQ}, q_{Max}[$):

$$U(q) = 2q\sqrt{\frac{s'^2}{m} + s'^2_{\mathrm{I}}\langle \mathrm{II}\rangle + u'^2_{\mathrm{T}}} \qquad u'_{\mathrm{T}} = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\}}/(\bar{R}N)$$

Example: Determination of total chromium in marine sediments:
$q_{\mathrm{LOQ}} = 7.5$ mg kg^{-1}

Results of the analysis of 5 sediment samples from a large river area:

Mass fractions (mg kg^{-1}): 47.93; 38.47; 42.02; 41.10; 53.04

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3. Analysis of a large item

(…)

Interval II ($[2q_{LOQ}, q_{Max}[$):

$$U(q) = 2q\sqrt{\frac{s'^2}{m} + s'^2_{\mathrm{I}}\langle \mathrm{II}\rangle + u'^2_{\mathrm{T}}} \qquad u'_{\mathrm{T}} = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\}}/(\bar{R}N)$$

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41.10; 53.04

	47.93
	38.47
	41.02
	41.1
	53.04
Mean	44.31
SD	6.01
RSD	13.6%
n	5

S'	6.07%

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3. Analysis of a large item

(…)

Interval II ($[2q_{LOQ}, q_{Max}]$):

$U(q) = 2q\sqrt{\frac{s'^2}{m} + s'^2_{\text{I}}\langle\text{II}\rangle + u'^2_{\text{T}}}$ $u'_{\text{T}} = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\}/(\bar{R}N)}$

Example: Determination of total chromium in marine sediments:

$q_{\text{LOQ}} = 7.5 \text{ mg kg}^{-1}$

Results of the analysis of 5 sediment samples from a large river area:

Mass fractions (mg kg^{-1}):
47.93; 38.47; 42.02;
41.10; 53.04

	47.93
	38.47
	41.02
	41.1
	53.04
Mean	44.31
SD	6.01
RSD	13.6%
n	5
S'	6.07%

$s' = 6.07\,\%$

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3. Analysis of a large item

(…)

Interval II ($[2q_{LOQ}, q_{Max}]$):

$U(q) = 2q\sqrt{\frac{s'^2}{m} + s'^2_{\text{I}}\langle\text{II}\rangle + u'^2_{\text{T}}}$ $u'_{\text{T}} = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\}/(\bar{R}N)}$

Example: Determination of total chromium in marine sediments:

$q_{\text{LOQ}} = 7.5 \text{ mg kg}^{-1}$

Result:

$$\bar{q} = \frac{44.31}{1.101} = 40.25 \text{ mg kg}^{-1}$$

$$U(q) = t(4; 95\%)40.25\sqrt{\frac{0.136^2}{5} + 0.0754^2 + \left(\frac{0.01885}{1.101}\right)^2}$$

$= 2.78 \cdot 40.25 \cdot 0.09837 = 11 \text{ mg kg}^{-1}$

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3. Analysis of a large item

(…)

Interval II ($[2q_{LOQ}, q_{Max}]$):

$U(q) = 2q\sqrt{\frac{s'^2}{m} + s'^2_{\text{I}}\langle\text{II}\rangle + u'^2_{\text{T}}}$ $u'_{\text{T}} = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\}/(\bar{R}N)}$

Example: Determination of total chromium in marine sediments:

$q_{\text{LOQ}} = 7.5 \text{ mg kg}^{-1}$

Result: Mean concentration of total chromium in the studied area of river sediments:

$$(40 \pm 11) \text{ mg kg}^{-1}$$

(for a confidence level of approximately 95 % using a $k = 2.78$)

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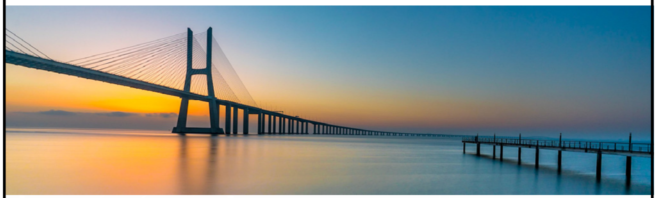
4. Exercise

Estimate the mean value of nitrite concentration in an area or Tagus river with uncertainty for a confidence level of 95 %.



4. Exercise

Estimate the mean value of nitrite concentration in an area or Tagus river with uncertainty for a confidence level of 95 %.

●●● Performance of the analysis of nitrite in a river water sample by segmented flow molecular spectroscopy (c_{LOQ} = 0.1 µmol L^{-1}):

Interval I: $[c_{LOD}, 2c_{LOQ}[$ (µmol L^{-1})		
s_r	s_I	u_T
0.0044	0.0107	0.0026

Interval II: $[2c_{LOQ}, (\ldots)[$ (%)		
s'_r	s'_I	u'_T
0.87	2.11	1.31

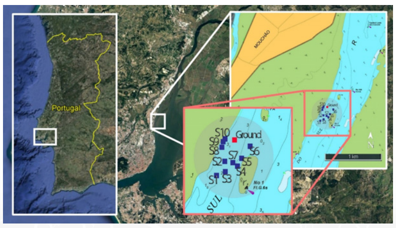
Note: No relevant systematic effects were observed in measurement.

C. Palma, C. Borges, R. Bettencourt da Silva, *Evaluation and optimisation of estuarine sampling uncertainty*, Isranalytica 2019, Tel Aviv, 22-23 January 2019.

4. Exercise

Estimate the mean value of nitrite concentration in an area or Tagus river with uncertainty for a confidence level of 95 %.

●●● Results of the analysis of 10 samples with known GPS coordinates:



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4. Exercise

Estimate the mean value of nitrite concentration in an area or Tagus river with uncertainty for a confidence level of 95 %.

●●● Results of the analysis of 10 samples with known GPS coordinates:

Sample	$c(NO_2)$ (µmol L^{-1})
S1	0.429
S2	0.459
S3	0.459
S4	0.480
S5	0.466
S6	0.393
S7	0.397
S8	0.490
S9	0.466
S10	0.459
Mean	0.450
SD	0.0329

C. Palma, C. Borges, R. Bettencourt da Silva, *Evaluation and optimisation of estuarine sampling uncertainty*, Isranalytica 2019, Tel Aviv, 22-23 January 2019.

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