EURACHEM/CITAC SCIENTIFIC WORKSHOP

MEASUREMENT UNCERTAINTY EVALUATION BASED ON IN-HOUSE VALIDATION DATA

Heavy metals in sediments

Hydrographic Institute
Division of Chemistry and Marine Pollution
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2022-10-26

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1- Introduction

"85 % of metals released into the aquatic environment are accumulated in sediments surface"

Z. Zhang, L. Juying, *EES*, **126** (2016) 94-101.

Element (mg kg^{-1})	Class 1	Class 2	Class 3	Class 4	Class 5
As	< 20	20 – 50	50 – 100	100 – 150	> 500
Cd	< 1	1 – 3	3 – 5	5 – 10	> 10
Pb	< 50	50 – 150	150 – 500	500 – 1000	> 1000
Ni	< 30	30 – 75	75 – 125	125 – 250	> 250

PORTUGAL, Portaria nº 1450/2007 de 12 de novembro do Ministério do Ambiente, do Ordenamento do Território e do Desenvolvimento Regional, *Diário da República*, 1ª série - nº 217/2007.

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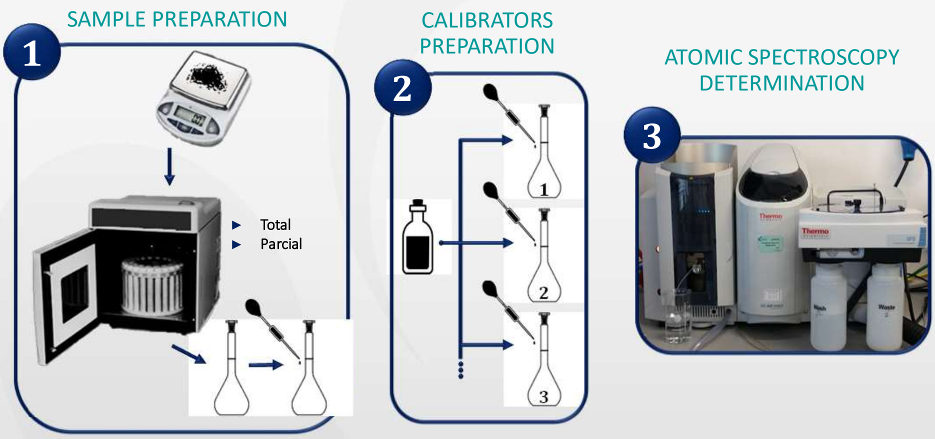
1- Introduction



1 – OSPAR COMMISSION, JAMP Guidelines for Monitoring Contaminants in Sediments, Agreement Ref.nº 2002-16 (2015) (111 pag.).
2 – EPA, Method 3051A – Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils, EPA, USA, 2007.

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1- Introduction

1. Introdução

Quasimeme Laboratory performance studies

✓ **QUASIMEME** (*Quality Assurance of Information from Marine Environmental Monitoring in Europe*)

$$\text{Z'-score} = \frac{\text{Mean from laboratory} - \textit{Consensus value (NDA mean)}}{\text{Total error}}$$

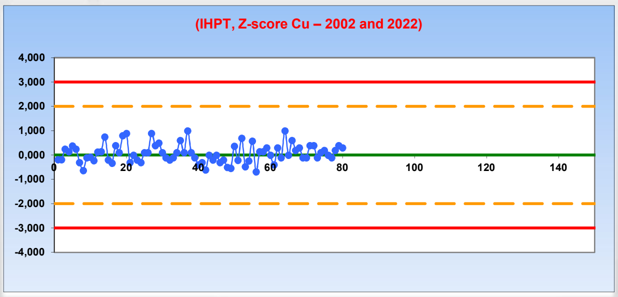
$$\text{Target error} = \frac{\text{Concensus value x Proporcional error(\%)}}{100} + 0{,}5 \text{ x Constant error}$$

$$\text{Total error} = \sqrt{U_X^2 + (Target\ error)^2}$$

|Z| < 2 satisfatory performance

2 < |Z| < 3 questionable performance

|Z| > 3 unsatisfatory performance



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1- Introduction

Measurement uncertainty concept

- The analysis of trace levels of analytes in complex matrices
  - Affected by matriz effects (due to the type of organic matter of the sediment)
  - Responsible for larger deviation between results
- Validation of the measurement procedure
  - Produce measurement results in an adequate analytical range with a measurement uncertainty smaller than the target (maximum admissible) uncertainty
  - Is necessary to take the variability of matrix effects into account
- Top-down evaluation based on in-house data:
  - Information collected during the validation of the measurement procedure
  - Involves quantifying and combining the uncertainty due to measurement precision and trueness
  - Takes the variability of matrix effects into account

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2- Top-down evaluation

2.1 Uncertainty evaluation steps:

Measurand definition

↓

Identification of uncertainty components

↓

Quantification of uncertainty components

↓

Components combination and subsequent expansion

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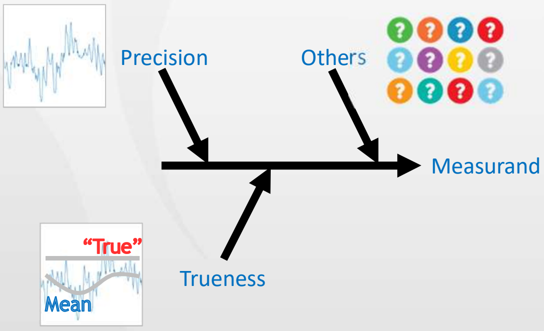
2- Top-down evaluation

2.2 Uncertainty components identification:



2- Top-down evaluation

2.3 Uncertainty components quantification

- **Precision:** intermediate precision standard deviation

- **Trueness:** mean recovery standard uncertainty and comparison with the ideal recovery

- **Others:** components not considered in the other two
  (e.g. sampling uncertain if relevant for the defined measurement)

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2- Top-down evaluation

2.4 Components combination and subsequent expansion:

$U = 2u_c$ (for approximately 95 % confidence level)

$U = 3u_c$ (for approximately 99 % confidence level)

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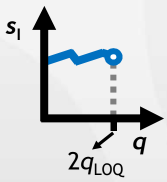
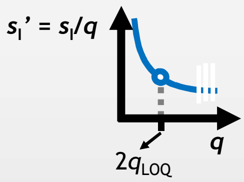
3- Uncertainty variation with the measured value

3.1 Precision variation



Absolute intermediate precision is constant below $2q_{LOQ}$



Relative intermediate precision is constant above $2q_{LOQ}$

q_{LOQ} – Limit of quantification

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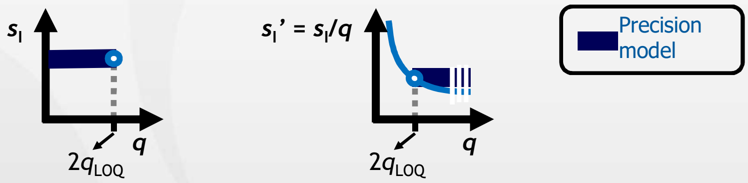
3- Uncertainty variation with the measured value

3.1 Precision variation:



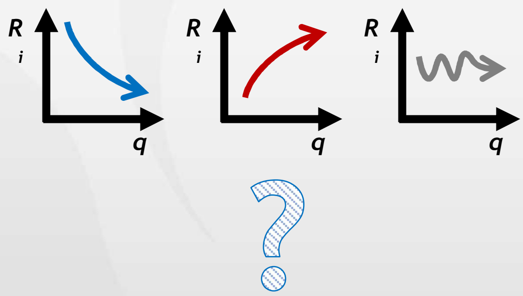
Absolute intermediate precision is constant below $2q_{LOQ}$

Relative intermediate precision is constant above $2q_{LOQ}$

q_{LOQ} – Limit of quantification

3- Uncertainty variation with the measured value

3.2 Recovery variation:



4- Top-down evaluations - equations

4.1 Precision uncertainty:

Interval I: [q_{LQD}, 2q_{LOQ}[

$$u_{P}\langle I\rangle = s_{I}\langle I\rangle = \sqrt{\frac{\sum_{e=1}^{E}(n_e-1)s_{Ie}^{2}}{\sum_{e=1}^{E}(n_e-1)}}$$

E estimates of s_I with (n_e-1) degrees of freedom.

Interval II: [2q_{LOQ}, (…) [

$$u'_{P}\langle II\rangle = s'_{I}\langle II\rangle = \sqrt{\frac{\sum_{f=1}^{F}(n_f-1)s'^{2}_{If}}{\sum_{f=1}^{F}(n_f-1)}}$$

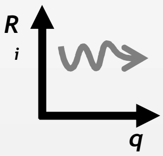
F estimates of s'_I with (n_f-1) degrees of freedom.

s_I and s'_I are the absolute and relative intermediate precision standard deviations.

4- Top-down evaluations- equations

4.2 Trueness uncertainty:

If recovery is approximately constant in the analytical interval:



u'_T - trueness relative standard uncertainty estimated for intervals I and II:

$$u'_T = \sqrt{\sum_{i=1}^{N}\{R_i^2[s'(R_i)^2 + u'(Q_i)^2]\} \Big/ (N\bar{R})}$$

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 ($\bar{R} = \sum R_i/N$).
(applicable to the analysis of reference items from proficiency tests)

4- Top-down evaluations- equations

4.2 Trueness uncertainty:

(…)

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

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

This assessment includes the comparison of the mean and ideal recovery:

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

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

4- Top-down evaluations- equations

4.3 Components combination and subsequent expansion:

Interval I: [q_{LQD}, 2q_{LOQ}[

$$U\langle I\rangle = 2\sqrt{u_P^2\langle I\rangle + (qu'_T\langle I\rangle)^2}$$

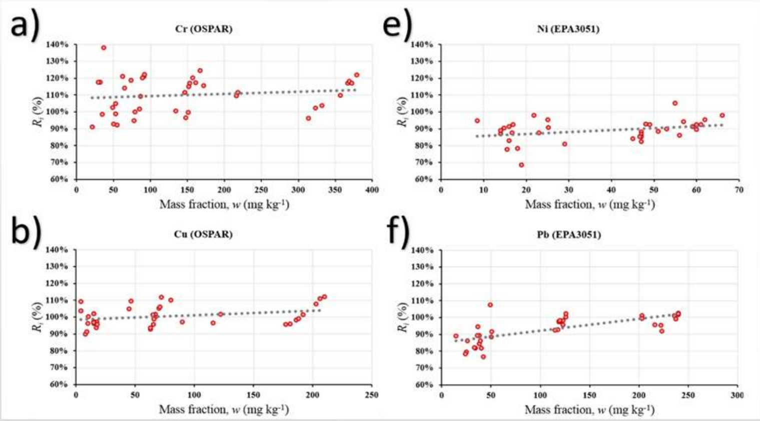
Interval II: [2q_{LOQ}, (…) [

$$U\langle II\rangle = 2q\sqrt{u'^2_P\langle II\rangle + u'^2_T\langle II\rangle}$$

5- Results

- **Determinations of total Cr, Cu, Li, Mn and Zn [1], and acid extractable Ni and Pb according to the EPA 3051A standard [2], in marine sediments.**

Recovery variation with the mass fraction



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5- Results

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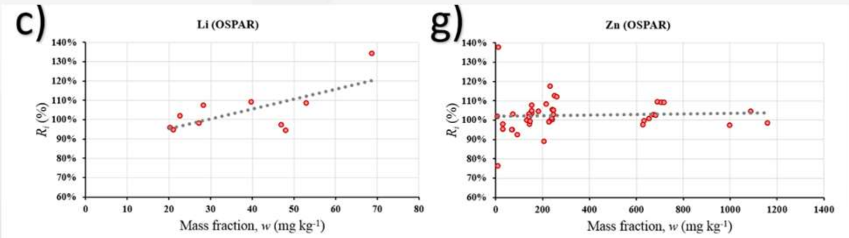

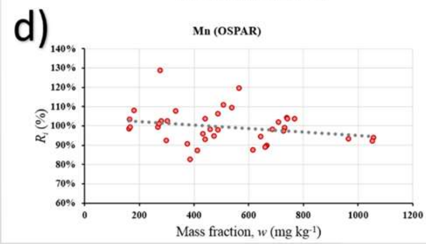

Approximately constant!

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5- Results

Element (procedure)	Cr (OSPAR)	Cu (OSPAR)	Li (OSPAR)	Mn (OSPAR)	Ni (EPA3051)	Pb (EPA3051)	Zn (OSPAR)
Matrix	Marine sediments						
w_{LOQ} (mg kg^{-1})	5	5	0.5	5	7.5	10	2
$u_P\langle I\rangle$(mg kg^{-1})	0.633	0.347	0.0675	0.680	1.18	1.08	0.159
$u'_P\langle II\rangle$(%)	6.33	3.47	6.75	6.80	7.97	6.37	3.97
u_T(absolute)	0.0189	0.0111	0.0395	0.0150	0.0131	0.0141	0.0145
$\bar{R}$ (%)	110	100	104	99.3	88.9	93.1	103
Is $\bar{R} \cong 100$ % ?	No	Yes	Yes	Yes	No	No	Yes
$u_c\langle I\rangle$(mg kg^{-1})	1.05	0.612	0.127	0.920	1.25	1.90	0.365
$u_c\langle II\rangle$	10.5	6.13	12.7	9.20	8.44	10.1	9.13
$U\langle I\rangle$(mg kg^{-1})	2.10	1.22	0.254	1.84	2.51	3.79	0.731
$U'\langle II\rangle$(%)	21.0	12.3	25.4	18.4	16.9	20.2	18.3

w_{LOQ} – Limit of Quantification in mass fraction units; $u_P\langle I\rangle$ and $u'_P\langle II\rangle$ – precision absolute and relative standard uncertainties below and above $2w_{LOQ}$, respectively; $u_c\langle I\rangle$ and $u'_c\langle II\rangle$ – combined absolute and relative standard uncertainties below and above $2w_{LOQ}$, respectively; $U\langle I\rangle$ and $U'\langle II\rangle$ – expanded absolute and relative standard uncertainties below and above $2w_{LOQ}$, respectively; CEC – number of estimated proficiency test results compatible with the reference value; $u_c^{tg}\langle I\rangle$ and $u'^{tg}_c\langle II\rangle$ – absolute and relative target standard uncertainties below and above $2w_{LOQ}$, respectively.

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5- Results

Assessment of metrological compatibility

Compatibility test

PT scheme	Ref. Value, wRef. (mg/kg)	u(wRef.) (mg/kg)	w(Lab.) (mg/kg)	d = w(Lab.) - wRef. (mg/kg)	u(w(Lab.)) (mg/kg)	Range (mg/kg)	Ud (k=3) (mg/kg)
QC1	66.63	0.77	68.00	1.37	6.09	1.37	18.42
QC2	15.25	0.36	15.60	0.35	1.40	0.35	4.33
QC3	10.00	0.25	10.58	0.58	0.95	0.58	2.94
QC4	10.50	0.22	10.54	0.04	0.94	0.04	2.91
QC5	41.20	2.14	38.57	-2.63	3.46	2.63	12.19
QC6	1.74	0.10	1.92	0.18	0.87	0.18	2.61
QC7	92.70	1.59	91.40	-1.30	8.19	1.30	25.03
QC8	9.88	0.42	11.70	1.82	1.05	1.82	3.38

$$|w_i - w_{\mathrm{Ref}j}| \leq t\sqrt{u^2(w_i) + u^2(w_{\mathrm{Ref}j})}$$

With $t = 3$ (99 % c.l.)

$|Dif.| \leq U_{Dif.}$

$|Dif.| > U_{Dif.}$

PT scheme	Compatibility
QC1	
QC2	
QC3	
QC4	
QC4	
QC5	
QC6	
QC7	
QC8	

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Compatibility external check (CEC)	20 in 20	20 in 20	15 in 15	20 in 20	20 in 20	20 in 20	20 in 20
$u_c^{tg}\langle I\rangle$(mg kg^{-1})	1.63	1.125	0.1125	0.675	1.44	2.25	1.500
$u'^{tg}_c\langle II\rangle$(%)	22.5	17.5	17.5	13.0	15.8	17.5	43.8

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4 - QUASIMEME, Quasimeme Laboratory Performance Studies – Programme 2019, Wageningen University, Wageningen, 2019.

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6- Conclusion

Developed top-down evaluation of measurement uncertainty:

- Two models of the measurement uncertainty were developed:
  - Interval I <2 LOQ
  - Interval II ≥2 LOQ

- Successfully applied to the determination of various elements in marine sediments

- The estimated relative expanded uncertainties are lower than the target uncertainty inferred from how z-score are calculated in QUASIMEME proficiency tests.

C. Palma, V. Morgado, R. J. N. Bettencourt da Silva, Top-down evaluation of matrix effects uncertainty, Talanta 192 (2018) 278-287.

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