EVALUATION OF MATRIX EFFECTS

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ABSTRACT

The measurement of trace levels of analytes in complex matrices, such as the copper in marine sediments, is frequently affected by matrix effects that vary with the analysed item. In some cases, the determination of the analyte in items of the same class, such as marine sediments, are affected by different matrix effects due to the different parameters that characterize the sediments: mineralogy, grain size, metal characteristics, pH, organic matter, and oxidation-reduction potential.

Since the measurement precision uncertainty does not reflect the impact of uncertainty components constant in estimated precision conditions on the measurement result, these effects are, partially or fully, quantified in the trueness uncertainty component.

This work presents a methodology to separately quantify the variability of matrix effects in complex measurements in order to decide about the need to improve measurements robustness to these effects. This methodology is based on the comparison of the mean recovery estimated from the analysis of various reference materials[1] and was applied to measurements of heavy metals in sediments by atomic spectrometry where measurements trueness was assessed from the participation in proficiency tests.

A — MEASUREMENT PERFORMANCE DATA

Limit of quantification, *w*(LOQ): 5 mg kg^{-1}

Table A1: Duplicate measurement results of independent analytical portions of the same sediment obtained under repeatability conditions.

Duplicates obtained under repeatability conditions:
(used to estimate analytical portions heterogeneity)

#	x_1	x_2	Mean, *m*	Absolute range, (for *m* < 2*LoQ)	Relative range, *A´* (for *m* ≥ 2*LoQ)
1	3.67	3.78	3.73	0.11	-
2	9.44	8.56	9.00	0.88	-
3	9.49	9.32	9.41	0.17	-
⋮	⋮	⋮	⋮	⋮	-
13	11.03	12.02	11.53	-	8.59%
14	11.17	11.24	11.21	-	0.62%
15	11.63	11.21	11.42	-	3.68%
16	10.84	11.31	11.08	-	4.24%
17	37.14	39.31	38.23	-	5.68%
18	41.79	39.63	40.71	-	5.31%
			Mean	0.291	3.22%

Table A2: Replicate measurements of a fortified blank sample obtained under intermediate precision conditions.

Intermediate precision	
Replicate analysis of a sample	
Range:	≥ 2LoQ
Date	**Value (mg/kg)**
07/03/2017	46.80
10/03/2017	48.37
17/03/2017	46.57
21/03/2017	46.74
24/03/2017	48.67
06/04/2017	46.74
⋮	⋮
Mean	48.30
St. Dev. (n≥10)	1.19
CV (n≥10)	2.45%

Measurement trueness (PT Results)

PT scheme	Ref. Value, wRef. (mg/kg)	u(wRef.) (mg/kg)	w(Lab.) (mg/kg)
A	3.74	0.21	3.88
B	3.76	0.22	4.11
C	1.14	0.18	1.22
D	8.93	0.33	8.03
E	1.18	0.13	1.16
F	⋮	⋮	⋮
Q	187.12	2.26	201.00
R	10.26	0.31	9.05

Table A3: Results from the participation in 18 proficiency tests required to quantify the trueness uncertainty.

B — ASSESSMENT OF RECOVERY VARIABILITY WITH DIFFERENT MATRICES

Recovery test Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
2	EQ	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
3	EQ	EQ	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
4	EQ	EQ	EQ	---	---	---	---	---	---	---	---	---	---	---	---	---	---
5	EQ	EQ	EQ	EQ	---	---	---	---	---	---	---	---	---	---	---	---	---
6	EQ	EQ	EQ	EQ	EQ	---	---	---	---	---	---	---	---	---	---	---	---
7	EQ	EQ	EQ	EQ	EQ	EQ	---	---	---	---	---	---	---	---	---	---	---
8	EQ	EQ	EQ	EQ	EQ	EQ	EQ	---	---	---	---	---	---	---	---	---	---
9	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	---	---	---	---	---	---	---	---	---
10	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	---	---	---	---	---	---	---	---
11	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	---	---	---	---	---	---	---
12	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	---	---	---	---	---	---
13	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	---	---	---	---	---
14	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	DIF	EQ	EQ	---	---	---	---
15	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	DIF	---	---	---
16	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	---	---
17	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	DIF	EQ	EQ	EQ	DIF	EQ	---
18	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ	EQ

EQ Metrologically compatible recovery values **(149 comparisons)**

DIF Not metrologically compatible recovery values **(4 comparisons)**

CALCULATION OF THE STANDARD UNCERTAINTY ASSOCIATED WITH THE RECOVERY, $u(\bar{R})$

$$\bar{R} = \frac{\sum_{i=1}^{N} R_i}{N}$$

$\bar{R}$: Mean recovery;
R_i: Recovery observed in the i^{th} proficiency test where $R_i = w_i / w_{\mathrm{Ref}i}$ (w_i and $w_{\mathrm{Ref}i}$ are the estimated and reference mass fractions where *i*=1 to *N*).

$$u(\bar{R}) = \sqrt{\sum_{i=1}^{N} \left\{ R_i^2 \left[\left(s'(w_i)\right)^2 + \left(u'(w_{\mathrm{Ref}i})\right)^2 \right] \right\} \Big/ N}$$

$s'(w_i)$: relative standard deviation of measurements intermediate precision estimated at w_i from models of the variation of the precision with w_i;
$u'(w_{\mathrm{Ref}i})$: relative standard uncertainty associated with $w_{\mathrm{Ref}i}$.

THE MASS FRACTION OF COPPER IN A SPECIFIC MARINE SEDIMENT SAMPLE ESTIMATED BY THE EPA 3050B STANDARD

C — EVALUATION OF THE MEAN RECOVERY

PT scheme (N = 18)	TRUENESS UNCERTAINTY — BEFORE assessing matrix effects variability *(using Table A2 for precision)*	AFTER assessing matrix effects variability *(using Table A3 for precision)*
A	32 %	23 %
B	32 %	23 %
C	105 %	74 %
D	14 %	9.7 %
E	101 %	70 %
F	7.8 %	5.9 %
G	12 %	6.7 %
	⋮	
R	12 %	8.4 %
$\bar{R}$	98.81 %	98.81 %
u_T	8.68 %	6.11 %
$t_{(cal)}$	0.136	0.193
$t_{\nu}^{0.95}$	2.11	

The mean recovery is metrologically equivalent to 100 %.

COMBINATION OF THE UNCERTAINTY COMPONENTS

Interval II: ≥ 10 mg kg^{-1}

$$U'_c = 2\sqrt{s'^2_{SS} + s'(R_i)^2 + u'(\bar{R})^2} = 2\sqrt{\left(\frac{0.032}{1.128}\right)^2 + (0.0589)^2 + (0.0611)^2} = 0.179$$

U'_c: relative expanded uncertainty;
s'_{SS}: relative standard deviation of measurement repeatability that includes the subsampling uncertainty.

Target Uncertainty U'^{tg}

U'^{tg} % (QUASIMEME) = 35 %

D — EXTERNAL QUALITY CONTROL OF THE MEASUREMENT UNCERTAINTY

Table D: Results from the participation in various international proficiency tests (PT) to assess the quality of the quantified measurement uncertainty.

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

ARE MASS FRACTION ESTIMATES METROLOGICALLY COMPATIBLE?

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

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	

FINAL REMARKS

- The developed methodology allowed the reliable evaluation of the uncertainty of measurements affected by matrix effects;
- The developed methodology can be used to calculated the precision due to matrix effects ($s'_M = \sqrt{s'^2_R - s'^2_I} = \sqrt{(0.0589)^2 - (0.0322)^2} = 0.0493$);
- Two models of the measurement uncertainty were developed for two mass fraction intervals (Interval I: < 2*w*(LOQ); Interval II: ≥ 2*w*(LOQ), presented in this poster).

1. R. Cordeiro, C. Rosa, R. Silva, *Accred. Qual. Assur.* (2018) 57-71,