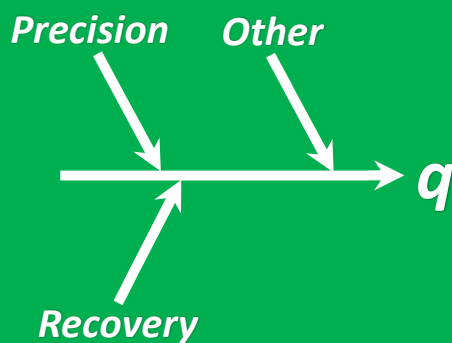


Implementing the new Eurachem/CITAC Guide in Excel



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Outline

Measurement uncertainty model Spreadsheet

C. Palma, V. Morgado, R. Bettencourt da Silva, *Talanta* 192 (2019) 278-287



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Uncertainty model

Interval I [q_{LOQ} , $2q_{LOQ}$]

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

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Uncertainty model

Interval I [q_{LOQ} , $2q_{LOQ}$]:

$$U = 2 \sqrt{\left(\frac{\bar{A}_{R(h)}\langle I \rangle}{1.128}\right)^2 + s_I^2\langle I \rangle - s_R^2\langle I \rangle + (q_{\square} \cdot u'_R)^2}$$

Mean range of duplicate results from the analysis of **heterogenous** samples under repeatability conditions **in Interval I**

Intermediate precision standard deviation from the analysis of **homogeneous** samples **in Interval I**

Repeatability standard deviation from the analysis of **homogeneous** samples **in Interval I**

Measured value **in Interval I**

Relative standard uncertainty of the mean recovery

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Uncertainty model

Interval I [q_{LOQ} , $2q_{LOQ}$]:

$$U = 2 \sqrt{\left(\frac{\bar{A}_{R(h)}\langle I \rangle}{1.128}\right)^2 + s_I^2\langle I \rangle - s_R^2\langle I \rangle + (q_{\square} \cdot u'_{\bar{R}})^2}$$

Mean range of duplicate results from the analysis of heterogeneous samples under repeatability conditions in Interval I

Intermediate precision standard deviation from the analysis of homogeneous samples in Interval I

Between-days variance

Standard deviation from the analysis of homogeneous samples in Interval I

Measured value in Interval I

Relative standard uncertainty of the mean recovery

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Uncertainty model

Interval I [q_{LOQ} , $2q_{LOQ}$]:

$$U = 2 \sqrt{\left(\frac{\bar{A}_{R(h)}\langle I \rangle}{1.128}\right)^2 + s_I^2\langle I \rangle - s_R^2\langle I \rangle + (q_{\square} \cdot u'_{\bar{R}})^2}$$

Mean recovery standard uncertainty from the analysis of reference materials without native analyte:

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

Slide 11 - « Evaluating the recovery component of measurement uncertainty »

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Uncertainty model

Interval I [q_{LOQ} , $2q_{LOQ}$]:

$$U = 2 \sqrt{\left(\frac{\bar{A}_{r(h)}\langle I \rangle}{1.128}\right)^2 + s_I^2\langle I \rangle - s_r^2\langle I \rangle + (q_{\square} \cdot u'_{\bar{R}})^2}$$

Mean recovery standard uncertainty from the analysis of reference materials without native analyte:

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Slide 11 - « Evaluating the recovery component of measurement uncertainty »

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Uncertainty model

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

$$U = 2q_{\square} \sqrt{\left(\frac{\bar{A}'_{r(h)}\langle II \rangle}{1.128}\right)^2 + s_I'^2\langle II \rangle - s_r'^2\langle II \rangle + u'^2_{\bar{R}}}$$

Measured value in Interval II

Mean RELATIVE range of duplicate results from the analysis of heterogeneous samples under repeatability conditions in Interval II

RELATIVE intermediate precision standard deviation from the analysis of homogeneous samples in Interval II

RELATIVE repeatability standard deviation from the analysis of homogeneous samples in Interval II

Relative standard uncertainty of the mean recovery



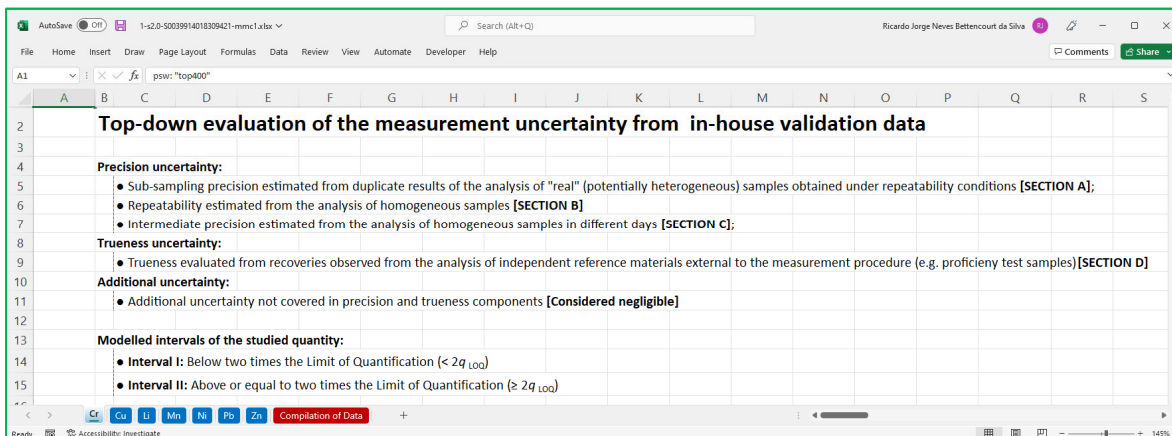
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Spreadsheet

Structure



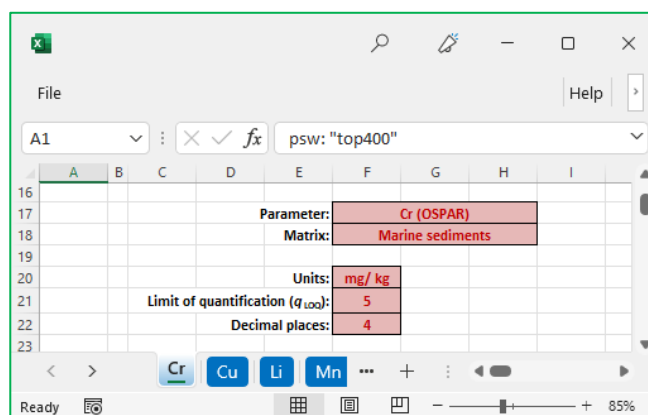
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Spreadsheet

Limit of Quantification



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Spreadsheet

Duplicate analysis of heterogeneous samples in Interval I and II
(repeatability conditions)

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Spreadsheet

Replicate analysis of homogeneous samples in Interval I and II
(repeatability conditions)

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Spreadsheet

Replicate analysis of homogeneous samples in Interval I and II
(intermediate precision conditions)

SECTION C:
Replicate analysis of homogeneous samples under intermediate precision conditions
(This uncertainty component is always relevant)

Symbols: $s_{<I>}$ and $s'_{<I>}$ are the absolute and relative standard deviations of measurements intermediate precisions in Interval I and II, respectively.

	Value	d.f. ($\nu=7$)
$s_{<I>}$	0.564762	37
$s'_{<I>}$	5.648%	37

Note: Estimated from $s'_{<I>} = 2 \cdot q_{LOQ}$

Maximum: 30 replicates per sample

Replicate results in Interval I			Replicate results in Interval II		
Sample G	Sample H	Sample I	Sample J	Sample K	Sample L
			56.99	54.64	
			56.45	56.90	
			55.90	57.58	
			55.09	57.00	
			55.04	58.84	
			55.13	61.10	
			55.95	59.62	
			55.67	52.96	
			54.42	54.70	

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Ready 85%

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Spreadsheet

Precision uncertainty in Interval I and II

Precision Uncertainty [Section(s) A&C]
Precision uncertainty estimated from the information collected on sections A, B and C (if relevant)

Symbols: $u_{<I>}$ and $u'_{<I>}$ are the absolute and relative standard uncertainties from measurement precision in Interval I and II, respectively.

	Value	For homogeneous Samples
$u_{<I>}$	0.632637	$u_{<I>}$: 0.564761523
$u'_{<I>}$	6.326%	$u'_{<I>}$: 5.648%

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Ready 85%

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Spreadsheet

Mean recovery and respective uncertainty

Initial Estimate

Mean recovery, R : 110.054%

Weighted mean recovery, R_w : 107.670%

u_r (absolute): 1.229%

Maximum: 50 Reference materials and 15 replicate analysis of each material

Units: mg/kg

Proficiency test scheme	Reference value, Q_i	$u(Q_i)$	Estimated value, q_i	Rep. 1 (Day a)	Rep. 2 (Day b)	Rep. 3 (Day c)	Rep. 4 (Day d)
Round 1	26.82	1.21	37.00				
Round 2	75.10	3.48	91.00				
Round 3	75.33	3.93	92.00				
Round 4	313.37	7.45	367.00				
Round 5	27.20	1.94	32.00				
Round 6	312.18	9.79	369.00				
Round 7	310.80	5.40	379.00				
Round 8	134.10	4.69	167.00				
Round 9	195.27	4.98	218.00				
Round 10	130.68	5.06	157.00				
Round 11	74.00	3.68	89.00				
Round 12	315.74	5.30	323.00				
Round 13	23.09	1.69	21.00				



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Spreadsheet

Compatibility of recoveries estimated for various Reference Materials

Comparison of recoveries: E - Metrologically equivalent recoveries, D - Metrologically DIFFERENT recoveries (coverage factor, $k = 3$)

PT Scheme	R_i	$u(R_i)$	Round 1	Round 2	Round 3	Round 4	Round 5	Round 6	Round 7	Round 8	Round 9	Round 10	Round 11	Round 12	Round 13	Round 14	Round 15	Round 16
Round 1	138.0%	9.961%	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
Round 2	121.2%	8.856%	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
Round 3	122.1%	9.390%	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
Round 4	117.1%	7.178%	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
Round 5	117.7%	10.687%	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
Round 6	118.2%	7.636%	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
Round 7	121.3%	7.206%	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
Round 8	124.5%	8.271%	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
Round 9	111.6%	6.918%	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
Round 10	120.1%	8.228%	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
Round 11	120.3%	9.054%	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
Round 12	102.3%	6.027%	D	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
Round 13	90.3%	8.404%	D	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
Round 14	111.6%	7.680%	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
Round 15	117.0%	7.055%	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E
Round 16	117.1%	8.764%	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E	E



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Spreadsheet

Combined standard uncertainty and decision on the need for recovery correction

The screenshot shows an Excel spreadsheet with the following data:

Combined standard uncertainty:		
	Real samples	Homogeneous samp.
$u_{c(D)}$	1.048502944	1.00900169
$u_{c(LD)}$	10.48503%	10.09002%

Percentage contribution:					
"Real" samples analysis:					
	Heter.	ME	Precision, P	Truness, T	P+T
Interval I	7.3929%	60.814%	97.219%	2.781%	100.000%
Interval II	7.3929%	60.814%	97.219%	2.781%	100.000%

Homogeneous samples analysis:					
	Heter.	ME	Precision, P	Truness, T	P+T
Interval I	-	65.6684%	96.9974%	3.0026%	100.000%
Interval II	-	65.6684%	96.9974%	3.0026%	100.000%

Decision table: Are results corrected for recovery? Yes



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Final remarks

- The presented MS-Excel file should be used after checking the respective algorithms

- The end-user of the spreadsheet must understand and agree with the formulas used.

Link:

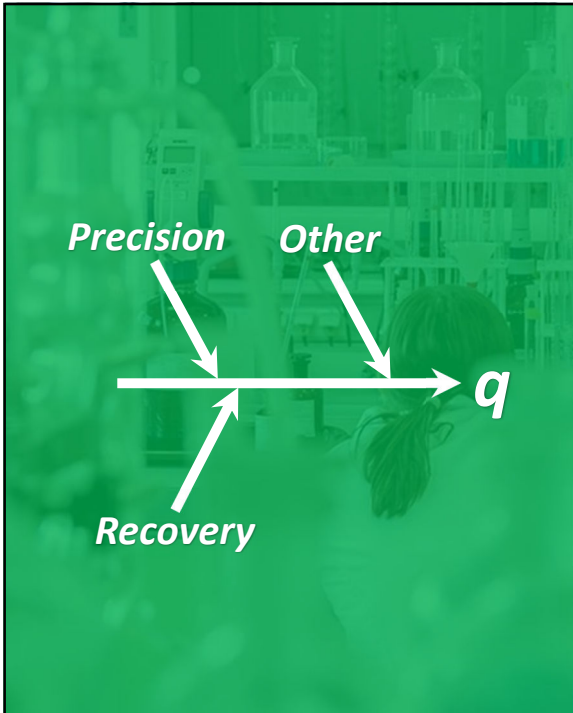
http://mechem.rd.ciencias.ulisboa.pt/wp-content/uploads/sites/99/2019/09/TopDown_MUE.xlsx



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Precision *Other*

Recovery

q



Thanks for your attention



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