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A Focus for Analytical Chemistry in Europe

PANCYPRIAN UNION OF CHEMISTS (PUC)
DIVISION OF QUALITY ASSURANCE

EURACHEM WORKSHOP

"Uncertainty in Qualitative and Quantitative Analysis"

A. G. Leventis House, University of Cyprus, Nicosia, CYPRUS, 29-30 May 2017

Is my uncertainty estimate reliable? Using data from CRMs, PT samples and standard methods

ISTITVTO SVPERIORE DI SANITÀ

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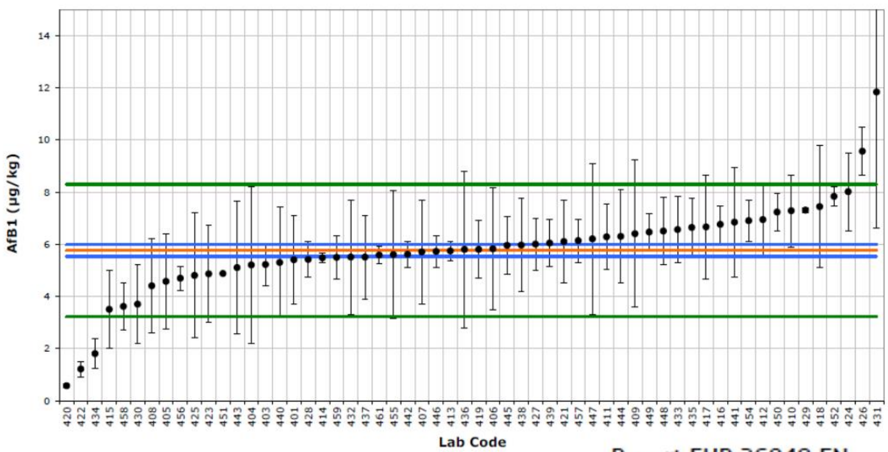
Figure 2: EURL Mycotoxins PT 2014: Aflatoxin B1 in copra - Sample A
Certified value: Xref = 5.76 µg/kg; Uref = 0.23 µg/kg (k=2); σ = 1.267 µg/kg



Report EUR 26849 EN

A common situation:
Laboratories report different uncertanties, not all of them overlapping with the certified value

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Measurement uncertainty

non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand,

based on the information used.

VIM 2.26

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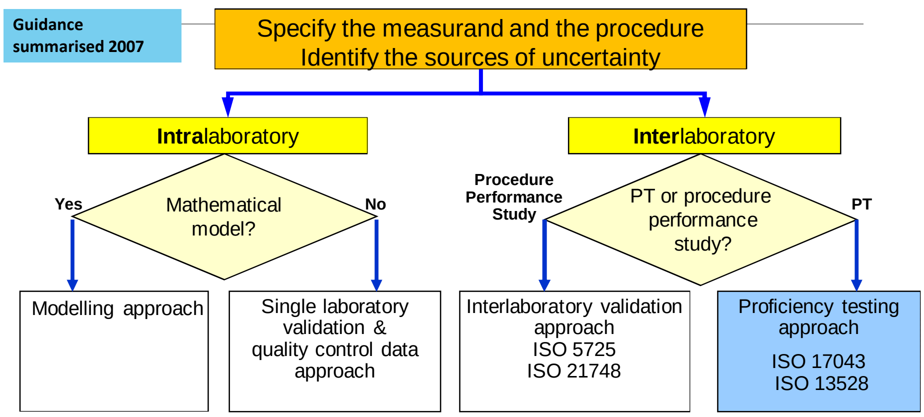
Approaches to evaluation of MU*



*Graph outline from: Eurolab Technical Report No. 1/2007www.eurolab.org.

The approaches available for estimating the uncertainty of measurement results use different information

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The Nordtest* approach main equations

$$u_c = \sqrt{u(R_w)^2 + u(bias)^2}$$

Within-laboratory reproducibility

Uncertainty of the estimate of the laboratory and the procedure bias

$$u(bias) = \sqrt{RMS_{bias}^2 + u(Cref)^2}$$

Bias variability

Average uncertainty of the reference value

* Handbook for calculation of measurement uncertainty in environmental laboratories (NT TR 537 - Edition 3.1)

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Assessing trueness

Definition

Closeness of agreement between the average of an infinite number of replicate measured quantity values and a reference quantity value

In practice, determine bias by means of:

- Comparison with a method of higher metrological order
- Analysis of an appropriate CRM
- Recovery studies of pure analyte added to samples
- Comparison with assigned values in collaborative studies / PTs

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Criticalities in trueness studies

Reliable references?

Commutability with real samples?

Can be put through the whole analytical process?

Covering concentration range?

Covering matrix range?

Uncertainty of the reference value?

Ideally, use several CRMs

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Choosing CRMs fit for the purpose

ERM®- BB422

FISH MUSCLE

Certified cadmium concentration (d.w.)
0,0075 mg/kg U (k=2) 0,0018 (24%)

Maximum Levels (Reg EC 1881):
0,005 – 3,0 mg/kg wet weight

DESCRIPTION OF THE MATERIAL

The sample consists of about 10 g of lyophilised, powdered fish muscle in a brown-glass vial with rubber insert and aluminium cap. Fish of the species *pollachius virens* (Saithe) was used for preparation of the material.

Consider concentration range, physical status,
need for additional measurements and their uncertainties

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Choosing CRMs fit for the purpose

BCR® – 696	PIG LIVER		
	Mass fraction (in reconstituted material)		Number of accepted sets of data p
	Certified value [2)] [mg/kg]	Uncertainty [3)] [mg/kg]	
Chlortetracycline[1)]	0.58	0.11	6

[2] certified by a group of laboratories [3] expanded uncertainty, k =2

Criteria for method performance – Reg. 657/2002/EC

$S_R < S_{Horwitz}$

At the level 0.58 mg /kg → $S_{Horwitz}$: 0.10 mg/kg

Compare the uncertainty of the certified value
With the requirements for method performance

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PT samples for "bias" assessment: advantages

Complementary to the use of traceable references (CRMs / reference measurements)

Larger availability

Covering the range of concentrations

Closer to real samples

When considerable experience exist, consensus values are a good estimate of the reference value

Limited cost

Collecting data via participation may take a long time, but surplus samples are often available from PT providers

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Conclusion

The reliability of MU estimates can be increased increasing the amount of information used,

E.g. for bias assessment use:

- several CRMs, carefully chosen
- PT samples as well

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INTERNATIONAL STANDARD

ISO 21748

First edition
2010-11-01

Guidance for the use of repeatability, reproducibility and trueness estimates in measurement uncertainty estimation

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Standard methods:
MU estimate according to ISO 21748:2010

Published performance data for:
- repeatability, reproducibility and bias

Consistency of laboratory bias and precision estimates with published performance data

Common belief: $U_{\text{rel}} = 2 \times RSD_R$

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Standard methods:
MU estimate according to ISO 21748:2010

Additional effects not included in the method study assessed and quantified
- See e.g. Example "Pesticides in bread" in QUAM, 2012

Evaluate measurement uncertainty from the reproducibility data, **combined, if necessary, with the uncertainty of the bias estimate and contributions from additional effects not included in the collaborative studies**

$$u_{\text{c rel}} = \sqrt{RSD_R^2 + u(bias)^2 + u_{x_i}^2} \Rightarrow u_{\text{c rel}} = RSD_R$$

Which reproducibility value?

Method	ISO 15673							
unit	mg / kg							
Element	Cd							
Sample	Carrot	Fish	Mushrooms CRM	Graham flour	Diet E CRM	Scampi	Mussels	Fish CRM Tort-2
Value (m)	0,3	0,87	0,46	0,033	0,52	0,08	1,7	28,3
s_R	0,03	0,09	0,03	0,01	0,04	0,013	0,16	3,56
RSD_R %	**8,8**	**11**	**6,9**	**32**	**8,1**	**16**	**9,5**	**13**

Often the value of some or most of the uncertainty contributions depends on the measurand value.

Three possible models of the relationship between reproducibility and measurand value are given in ISO 5725-2:1994

$$\hat{s}_R = bm$$

$$\hat{s}_R = a + bm$$

$$\hat{s}_R = cm^d$$

m = concentration

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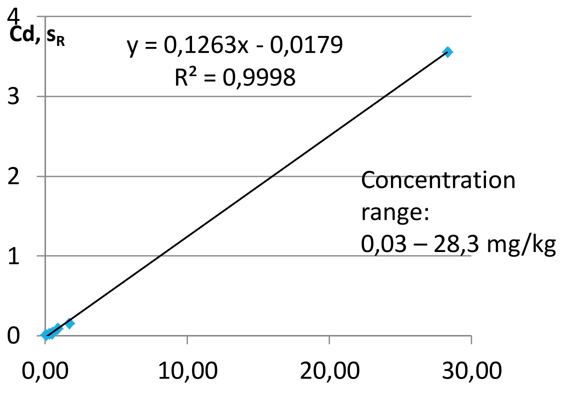
A linear model



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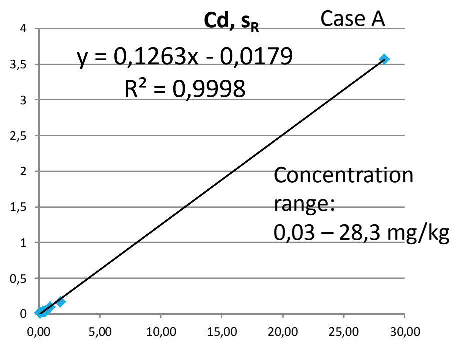
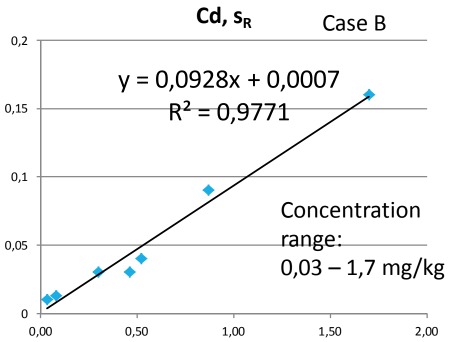
Different outcomes





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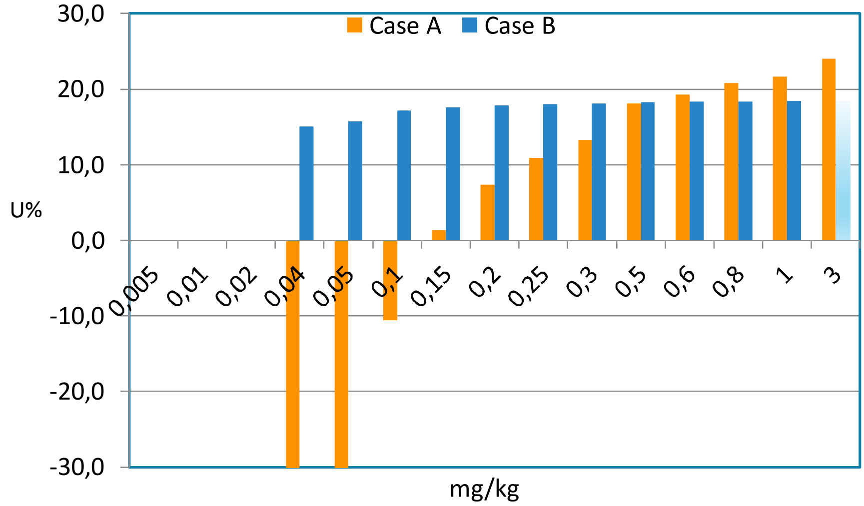

Estimated U% at the maximum levels for Cd in food (Reg EC 1881)

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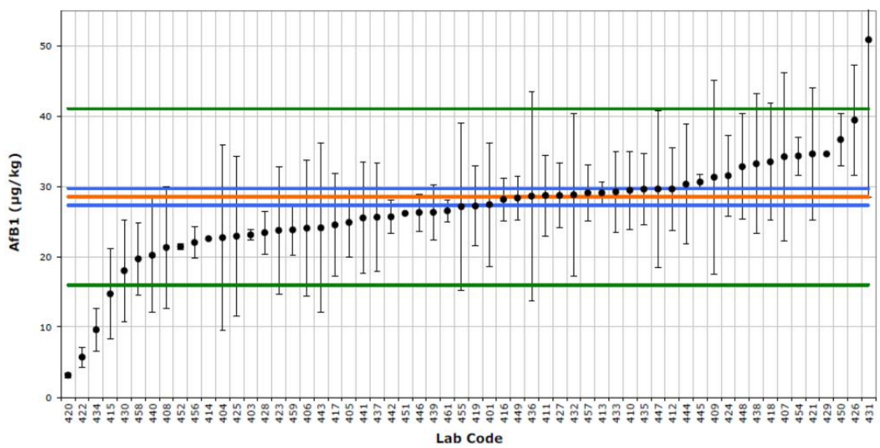
Conclusion

Using a standard method does not «automatically» provide a reliable measurement uncertainty estimate just off the shelf.

A crtical assessment is still required.

Figure 3: EURL Mycotoxins PT 2014: Aflatoxin B1 in copra - Sample B
Certified value: Xref = 28.5 µg/kg; Uref = 1.5 µg/kg (k=2); σ = 6.27 µg/kg



Report EUR 26849 EN

What can be learned from reporting the measurement uncertainty of the participant's result?
(See also Eurachem leaflet "How can proficiency testing help my laboratory?")

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Is my uncertainty estimate too small? zeta-scores in PTs

ζ-scores

- Increasingly used as additional information in Proficiency testing
- May be used for scoring if assigned values independent from participants' data
- Help participants to check the reliability of their MU estimate

$$\zeta = \frac{(x_i - x_{pt})}{\sqrt{u^2(x_i) + u^2(x_{pt})}}$$

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zeta-score interpretation

Performance
Ò2
> 2 but Ò3
> 3

Code	Result	z-score	ζ-score
418	7.44	1.3	1.4
419	5.8	0.0	0.1
420	0.57	-4.1	-44.5
421	6.1	0.3	0.4
422	1.21	-3.6	-24.1
423	4.86	-0.7	-1.0
424	8.01	1.8	3.0
425	4.8	-0.8	-0.8
426	9.56	3.0	7.9
427	6	0.2	0.5
428	5.41	-0.3	-1.0
429	7.3	1.2	12.8
430	3.7	-1.6	-2.7
431	11.83	4.8	2.3
432	5.5	-0.2	-0.2

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What about too LARGE uncertanties?

Target measurement uncertainty

measurement uncertainty specified as an upper limit and decided on the basis of the intended use of measurement results

Where requirements for target measurement uncertainties exist,

they are sometimes used as such

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Toward MU estimates fit for the purpose (ISO 13528:2015)

Proficiency test providers to warn participants reporting

$u_{lab} << u(x_{pt})$

$u_{lab} >> 1.5\ s^*$

s* = robust standard deviation of participants' data

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Conclusion

The reliability of MU estimates can be increased by at least:

- increasing the amount of information used, e.g. using more CRMs and PT samples to assess the bias component
- Assessing standard methods critically
- Participating in PT and making the most of it

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Thank you for your attention!

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