Determination of the standard deviation for proficiency assessment from past participant's performances

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Introduction

The Centre of Toxicologie du Québec (CTQ) [1] is a public organization that has been offering human toxicology expertise (environmental, clinical and occupational) to the provincial health network of Quebec (Canada) as well as to external clients from around the world since 1972. Our laboratory has ISO/IEC 17025 and ISO 17043 accreditations. The CTQ is part of the Institut National de Santé Publique du Québec (INSPQ).

Since 1979, the CTQ has been operating permanent external quality assessment schemes that enable participating laboratories to evaluate the accuracy and precision of their analytical methods on a continuous basis. Approximately 250 laboratories from over 30 countries participate in these schemes. We offer biological proficiency testing materials (PTMs) in human matrices such as blood, serum, urine, blood and hair covering a wide variety of elements such as Ag, Al, As, Ba, Bem Bi, Cd, Co, Cr, Cs, Cu, F, Hg, Hg, I, Mn, Mo, Ni, Pb, Pt, Sb, Se, Sn, Te, Th, Tl, U, V, W and Zn, and over 30 organic contaminants in human serum including PCBs, organochlorinated pesticides, PBDEs (flame retardants) and perfluorinated compounds.

Our Proficiency Testing Programs

• **PCI** – Interlaboratory Comparison Program for metals in biological matrices
- Over 130 laboratories per round
- Participants can use any method
- Participants receive six rounds every year each containing three PTMs per analyte
- Some PTMs are shipped in duplicate to evaluate analytical reproducibility

• **QMEQAS** – Quebec Multielement External Quality Assessment Scheme
- ca. 60 laboratories per round equipped with multi-elemental capabilities (i.e ICP-MS)
- Participants receive three rounds every year each containing three PTMs

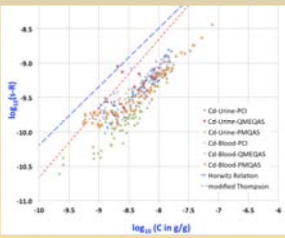
• **PMQAS** – Priority Metals Quality Assessment Scheme
- Participants = US state laboratories
-All participants equipped with the same brands of instruments (ICP-MS), same analytical methods and same standards, thus providing similar analytical environment for greater comparability
- Measurands = Metals in blood and urine

• **AMAP** – Ring test for persistent organic pollutants in human serum
- 30 Laboratories participating in the Arctic Monitoring and Assessment Program

Methodology

-A huge dataset was collected from previous PTs (3 PTs; 30 elements; 4 matrices; 30 to 130 participants)
-We focus today on Hg, Cd and Pb results obtained in blood and urine
-We compiled all the relevant X_{ref} and σ_{PT} - computed according robust statistics of ISO 13528

What do we observe ?



- *We first compared (i) the Horwitz [2] and (ii) the Thompson's modified [3] models to our reproducibility standard deviations (see Cd in the left graph)* ➔ *no satisfactory agreement*
- *Several graphical plots were generated*
- *Various fitting models were tested (linear, power curves)together with the intuitive/empirical uncertainty function suggested by Thompson [4, 5]*
- *The results of the latter fit is shown in the right graphs for PMQAS-Cd-Blood dataset (note: various x & y axis used)*
- *The model equation fits well the experimental data*
- *This model was systematically applied to the other data selected. The fitting parameters are summarized in the Table below.*

					Calculated		= α/β
element	**matrix**	**ILC**	**N**	**Conc Range (g/g)**	**α**	**β**	**Threshold**
	Blood	PCI	63	(0,11 - 1,5) E-8	2,0E-10	8,3%	2,4E-09
Cd		PMQAS	75	(0,06 - 7,9) E-8	1,5E-10	5,0%	3,0E-09
		QMEQAS	22	(0,05 - 1,3) E-8	1,5E-10	7,6%	2,0E-09
	Urine	PCI	63	(0,06 - 1,6) E-8	1,5E-10	7,6%	2,0E-09
		PMQAS	60	(0,02 - 1,8) E-8	3,0E-11	5,0%	6,0E-10
		QMEQAS	24	(0,14 - 1,3) E-8	1,0E-10	7,6%	1,3E-09
	Blood	PCI	63	(0,18 - 8,3) E-8	5,0E-10	12,0%	4,2E-09
Hg		PMQAS	75	(0,01 - 1,2) E-7	4,0E-10	5,5%	7,3E-09
		QMEQAS	22	(0,15 - 6,1) E-8	8,0E-10	7,5%	1,1E-08
	Urine	PCI	63	(0,02 - 2,6) E-7	9,0E-10	11,0%	8,2E-09
		QMEQAS	24	(0,40 - 9,2) E-8	9,0E-10	15,0%	6,0E-09
	Blood	PCI	63	(0,17 - 8,4) E-7	3,0E-09	6,3%	4,8E-08
Pb		PMQAS	75	(0,02 - 1,4) E-6	3,0E-09	5,2%	5,8E-08
		QMEQAS	22	(0,24 - 5,6) E-7	2,0E-09	6,3%	3,2E-08
	Urine	PCI	63	(0,12 - 7,7) E-7	3,0E-09	7,5%	4,0E-08
		PMQAS	60	(0,004 - 4) E-7	1,5E-10	3,9%	3,8E-09
		QMEQAS	24	(0,02 - 1,0) E-6	2,0E-09	6,3%	3,2E-08

The work flow

Input data derived from
- Three PTs : PMQAS, PCI and QMEQAS
- Three analytes : Cd, Hg and Pb
- Two matrices : Blood and Urine

Four graphical representations:

(a) Reproducibility Relative Standard Deviation (RSD_R in %) vs. concentration (C) expressed in g/g, according to Horwitz [2]; *with the characteristic trumpet shape*

(b) Reproducibility Standard Deviation (s_R) vs. C, as presented by Thompson *et al.* [4, 5]; *seemingly linear at high concentrations*

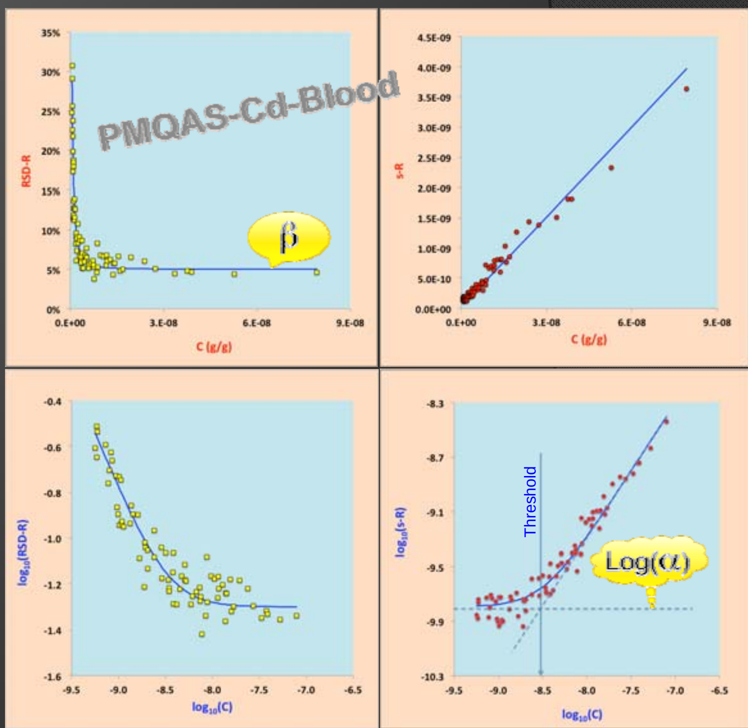
(c) $\log_{10}(RSD_R)$ vs. $\log_{10}(C)$

(d) $\log_{10}(s_R)$ vs. $\log_{10}(C)$, as suggested by Thompson [3]

Fit the model equation

suggested by Thompson [5]

$$s_R = \sqrt{\alpha^2 + (\beta * C)^2}$$



Conclusions

- Observed reproducibility standard deviations (s_R) below the Horwitz and the Thompson-modified curves
- Lowest s_R for PMQAS - as expected; all participants use the same instrumentation and the same standard methods
- Thompson's empirical "uncertainty function" confirmed for all the data investigated. Knowing the value of the measurand, we can set *a priori* $\sigma_{PT} = s_R$ (no need to apply Algorithm A of ISO 13528)

Next steps

- Apply this methodolgy to the remaining datasets available (other PTs/Elements/Matrices)
- Consider using PMQAS consensus values as references for other PT programs (when possible)

Bibliography

[1] www.inspq.qc.ca/ctq/page
[2] M. Thompson, *Analyst* 125 (2000) 385
[3] W. Horwitz, *et al.*, *J. Assoc. Off. Anal. Chem.* 63 (1980) 1344
[4] M. Thompson, B. J. Coles, *Accred. Qual. Assur.* 16 (2011) 13
[5] M. Thompson, *Trends in Anal. Chem.* 30 (2011) 1168

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