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Is my bottom-up uncertainty estimation on metal measurement adequate?

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Abstract: *Is the estimated uncertainty under GUM recommendation associated with metal measurement adequately estimated? How to evaluate if the measurement uncertainty really covers all uncertainty that is associated with the analytical procedure? Considering that, many laboratories frequently underestimate or less frequently overestimate uncertainties on its results; this paper presents the evaluation of estimated uncertainties on two ICP-OES procedures of seven metal measurements according to GUM approach. Horwitz function and proficiency tests scaled standard uncertainties were used in this evaluation. Our data shows that most elements expanded uncertainties were from two to four times underestimated. Possible causes and corrections are discussed herein.*

Keywords: uncertainty estimation, metal analysis, ICP-OES, dark uncertainty

1. INTRODUCTION

Expanded uncertainty (U) estimation according to GUM [1] approach is widely applied although time-consuming. Often this procedure is criticized because not all uncertainty sources are covered on its budget [2, 3, 4, 5] Dark uncertainty is a concept defined [3, 5] as the uncertainty not seen at all and therefore unaccounted in the measurement uncertainty estimation budget. So, the emerging question is how to evaluate if the uncertainty estimation was realistic or adequate? Several laboratories follow the procedure and do not evaluate its uncertainty results by other means.

Horwitz [4] treated large amount of analytical data and recommended four approaches to answer this question. These approaches are:

- To run sufficient replicates,
- To reevaluate and revise in details previous uncertainty estimation budget,
- To examine carefully laboratory proficiency test results,
- To compare the uncertainty estimation with Horwitz function results [6].

The present paper aimed to evaluate GUM estimated uncertainty of seven metals measurement by ICP-OES in two different matrixes [7, 8], with different analysts and distinct analytical data. Horwitz approach was used in this work to verify if GUM uncertainty estimation adequately cover all measurement uncertainty.

2. METHODS/EXPERIMENTAL

The GUM approach that estimate uncertainty on seven metal measurement (Ba, Cd, Cr, Cu, Fe, Mn and Ni) on wastewater and superficial water by ICP-OES were evaluated. Method 1 and Method 2 were developed and applied to superficial water samples [9] and to wastewater [10] respectively, and details from the uncertainty estimation can be found elsewhere [7, 8]. Despite the fact that both

works were developed at CQMA/IPEN, all analytical data were performed separately and therefore are independent. Both methods chosen the same wavelengths for each element measurement.

2.1. Horwitz approach

All four approaches that Horwitz [4] recommends, to verify uncertainty estimation procedure, are discussed in this paper. Some remarks are presented to each recommended step.

- To increase the number of replicates will not change the true value [4], but only increase the confidence on the estimated interval from the true value. In the later uncertainty estimation, this step is not feasible. This must be accounted on the experimental design of the uncertainty estimation procedure.
- Previous studies detailed the uncertainty budget [7, 8], so the uncertainty values estimated with the GUM approach will solely be confronted with complementary data.
- Minimum of two years PT results of Ba (n =8), Cr (n = 12), Cu (n = 4), Fe (n = 12), Mn (n = 6) and Ni (n = 12) helped to evaluate laboratory uncertainty through the Scaled Standard Uncertainty – SSU [11] (see eq. 1). The PT provider is EPTIS registered with ISO17043 accreditation [12].
- The Horwitz formula (see eq. 2) was previously extensive tested [4, 5, 13, 14] and herein applied to Method 1 and 2 in order the estimated uncertainty.

$$SSU = \frac{u(y)}{\hat{\sigma}_R} \qquad \textit{Eq. 1}$$

Where: u(y): estimated uncertainty; $\hat{\sigma}_R$: standard uncertainty of the correspondent element PT's

$$RSD = 2 \times C^{-0.15} \qquad \textit{Eq. 2}$$

Where: RSD: Relative standard deviation in %;C: mass to mass fraction, i.e. 1mg L^{-1} = 10^{-6} g g^{-1}.

3. RESULTS AND DISCUSSION

Method 1 and 2 summary of expanded uncertainty (U, k=2) are presented in Table 1 and 2 respectively. With each method concentration range, the relative standard deviation expected by Horwitz function was calculated and ranged between 11 and 16 % to method 1 and between 11 and 25 % to method 2. While the U (k=2) ranged between 3 and 13% to method 1 and 5 to 12% to method 2. Horwitz coverage was calculated as the ratio of each method U (k=2) to expected RSD from Horwitz function. By that way, U(k=2) corresponded roughly to 25 to 80% of all variability expected from Horwitz function in method 1 and to 24 to 60% in method 2, with only one element (Fe) with 106% uncertainty coverage. However, as an empiric method we understand that interpretation needs to be tested.

The SSU evaluation, applied as a secondary test, considers that if GUM approach covers most of measurement uncertainty, then SSU = 1 or a close value. As presented in Table 1 and 2, most values of method 1 SSU ranged from 0.17 to 0.31 with a close to unity value (0.93) only to Cu. Method 2 SSU ranged from 0.25 to 0.62. GUM uncertainty and reproducibility studies tested by Walsh et al. [2] and Thompson [5] presented SSU < 1, often uncertainty was underestimated by a factor of 2. The underestimation factor in Method 1 and 2 seems to vary from 4 to 2.5 (as SSU = 1). The cause of this behavior could be a shorter time in reproducibility studies than ideally required.

However, different laboratories, procedures and different analytical techniques seem to face same results [2, 5, 4], as obtained in Method 1 and 2. Which indicates not all variability associated with chemical measurement could be explained with GUM procedure. To solve this issue, a larger coverage factor k could be more suitable. Horwitz and SSU evaluations were adequate to identify a better coverage factor.

Table 1: Method 1 summary of expanded uncertainty estimation (GUM, Horwitz function and SSU).

Element	Major Uncertainty component	U % (k=2)	Concentration range (mg/L)		RSD% by Horwitz Function	Horwitz Coverage %	SSU
Ba	Analytical curve	3	0.10	10.00	11	27	0.25
Cd	Analytical curve	5	0.01	1.00	16	38	n.a.
Cr	Standard preparation	4	0.01	1.00	16	25	0.31
Cu	Recovery	13	0.01	1.00	16	81	0.93
Fe	Recovery	5	0.10	10.00	11	44	0.17
Mn	Standard preparation	4	0.01	1.00	11	35	0.27
Ni	Standard preparation	4	0.01	1.00	16	25	0.17

Table 2: Method 2 summary of expanded uncertainty estimation (GUM, Horwitz function and SSU).

Element	Major Uncertainty component	U % (k=2)	Concentration range (mg/L)		RSD% by Horwitz Function	Horwitz Coverage %	SSU
Ba	Recovery	5	0.10	10.00	11	44	0.42
Cd	Recovery	6	0.01	0.05	25	24	n.a.
Cr	Recovery	8	0.03	3.00	14	59	0.62
Cu	Recovery	7	0.03	3.00	14	52	0.50
Fe	Recovery	12	0.10	10.00	11	106	0.40
Mn	Recovery	5	0.01	1.00	16	31	0.33
Ni	Recovery	6	0.01	1.00	16	38	0.25

4. CONCLUSION

Despite worldwide use and largely debated to estimate measurement expanded uncertainty, GUM approach could easily do not cover all uncertainty sources. This work data with detailed uncertainty budget, applied to two different matrixes, seven elements, performed by different analysts with extensive reproducibility and recovery studies, when confronted with much simpler models seems to underestimate uncertainties by a factor from 2 to 4. Therefore, to prevent this effect it is recommended to apply other uncertainty estimation procedures that could guide the analyst and the laboratory find a more suitable uncertainty estimation value, and at the end, if required, to expand the usual coverage factor.

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