Uncertainty Estimation of Metals and Semimetals Determination in Wastewater by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

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Abstract: The measurement uncertainty is a parameter that represents the dispersion of the results obtained by a method of analysis. The estimation of measurement uncertainty in the determination of metals and semimetals is important to compare the results with limits defined by environmental legislation and conclude if the analytes are meeting the requirements. Therefore, the aim of this paper is present all the steps followed to estimate the uncertainty of the studied method. Measurement uncertainty obtained was between 4.6 and 12.2% in the concentration range of $mg.L^{-1}$.

Keywords: Measurement Uncertainty. Metals. Wastewater. Sources of Uncertainty.

1. INTRODUCTION

According to the International Vocabulary of Metrology (VIM) measurement uncertainty is a non-negative parameter characterizing the dispersion of the quantity values that is attributed to a measurand [1]. To carry out this estimation, it is necessary to follow some steps such as: to determine the measurement model; evaluate the sources of uncertainty; estimate the uncertainty in each step of the method and determine the combined and expanded uncertainty, regarding the confidence interval wanted [2].

The estimation of measurement uncertainty is important to express how precise is the method used and whether the results obtained are really meeting the needs of environmental legislations or other limits.

2. OBJECTIVE

This work aims to demonstrate the steps used to estimate the measurement uncertainty in the determination of metals and semimetals (B, Sn, Cd, Ba, Cr, Cu, Fe, Mn, Ni, Pb and Ni) in wastewater, after acid digestion and analysis by ICP-OES.

3. MEASUREMENT UNCERTAINTY

It is necessary to perform the entire method study, in order to estimate the measurement uncertainty. In this case, the method validation was performed, and all the calculations needed are described below.

1.1. Measurement Model

The first step was to determine the measurement model used to obtain the measurand. From the equation 1, it was found feasible to raise the sources of uncertainty that influences in the quantification of metals and semimetals in wastewater, using the method studied.

$$C = \frac{(CA \; x \; V_{final})}{V_{inicial}} . \frac{1}{R} \qquad (1)$$

Where: C = Concentration in the sample ($mg.L^{-1}$); CA = Concentration of the element according to

the calibration curve (mg.L^{-1}); V_{final} = Final volume of the sample (50 mL); $V_{initial}$ = Initial volume of the sample (45 mL); R = Recovery of the method.

1.2. Sources of Uncertainty

The uncertainty sources are presented with a quality tool called Ishikawa Diagram in Figure 1. All stages of Sample preparation and analysis were considered [6].

The contribution of each source of uncertainty is described in the next items.

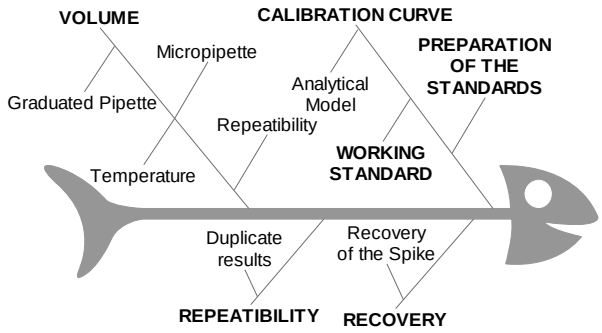

FIGURE 1: Ishikawa Diagram to the studied method

1.3. Volume Uncertainty

In this step, all sources of uncertainty that contribute to metal concentration dispersion were considered. Part of the uncertainty come from the volume measurement in the acid digestion process. The initial volume of sample is measured using a graduated pipette (two aliquots - 25 mL and 20 mL), after that, two acids are add to the sample, measured with a micropipette. The first source of uncertainty considered was the maximum variation of 5°C of temperature in the laboratory. This uncertainty was calculated according to equation 2.

$$\mu(V_T) = \frac{\Delta T . Q . V}{\sqrt{3}} \qquad (2)$$

Where: ΔT = Variation of temperature in the laboratory (°C); Q = Expansion coefficient of water (0.000124°C^{-1}); V = Volume and $\sqrt{3}$ = considering rectangular distribution.

The second source of uncertainty considered was the uncertainty of the glassware, calculated according to equation 3.

$$\mu(V_P) = \frac{\mu(cert)}{\sqrt{6}} \qquad (3)$$

Where: $\mu(cert)$ = Uncertainty informed by the producer and $\sqrt{6}$ = considering triangular distribution.

The last source of uncertainty of volume considered was the repeatability of the measure. In this case, ten measures were carried out, using all glassware, and the uncertainty was calculated according to equation 4.

$$\mu(V_{repe}) = \left(\frac{s}{\sqrt{n}}\right) \qquad (4)$$

Where: s = Standard deviation of the measures and n = Number of measures.

The volume uncertainty were combined as presented in equation 5.

$$\mu(V_X) = \sqrt{\mu(V_T)^2 + \mu(V_P)^2 + \mu(V_{repe})^2} \qquad (5)$$

1.4. Calibration Curve: Preparation of Standards

All the standards used to build the calibration curves were prepared from a multielemental working standard (WS), prepared from monoelemental certified standards. To estimate the uncertainty of the preparation of WS, firstly was estimated the uncertainty of volume, as presented before, and the other sources are presented in equation 6.

$$\mu(C_{WS}) = \left[\sqrt{\left(\frac{\mu V_P}{V_P}\right)^2 + \left(\frac{\mu V_{VF}}{V_{VF}}\right)^2 + \left(\frac{\mu C_{std}}{C_{std}}\right)^2}\right] . C_{WS} \qquad (6)$$

Where:

μV_P = Uncertainty of the volume used of the certified standard; V_P = Volume used of the certified standard; μV_{VF} = Uncertainty of the volumetric flask; V_{VF} = Volume of the volumetric flask; μC_{std} = Uncertainty informed in the certificate of the standard; C_{std} = Concentration of the standard (informed in the certificate); C_{WS} = Final concentration of the working standard.

In equation 7, it is presented the method used to estimate the uncertainty of each standard used to build the calibration curve.

$$\mu(C_{PX}) = \left[\sqrt{\left(\frac{\mu V_P}{V_P}\right)^2 + \left(\frac{\mu V_{VF}}{V_{VF}}\right)^2 + \left(\frac{\mu C_{WS}}{C_{WS}}\right)^2}\right] . C_{SX} \quad (7)$$

Where: C_{SX} = Final concentration of each standard.

Results were presented as a percentage, and the greater one was found to be the preparation of the calibration curve uncertanty.

1.5. *Calibration Curve: Analytical Model*

The uncertainty of the analytical model was estimated using the calculation presented in the EURACHEM Guide (equation 8) [1].

$$\mu(C_X) = \frac{S}{B_1}\left[\sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(C_X - \bar{C})}{S_{xx}}}\right] \quad (8)$$

Where: S = Residual standard deviation; B_1 = slope; p = Number of measures to determine C_X; n = Total number of replicates; C_X = Sample concentration; $\bar{C}$ = Calibrations average and $S_{xx} = \sum_{i=1}^{n}(C_i - \bar{C})^2$ where C_i = Concentration obtained from the calibration curve.

1.6. *Repeatability Uncertainty*

To estimate the repeatability uncertainty was used the equation 9.

$$\mu(Repe) = \left(\frac{Máx\ RSD}{\sqrt{n}}\right) \quad (9)$$

Where: $Máx\ DPR$ = Greater value of relative standard deviation of the interval;

In this work, data from the analysis performed in 2013 and 2014 applying this method were used.

1.7. *Recovery Uncertainty*

To estimate the recovery uncertainty the equation 10 was used.

$$\mu(Rec) = \left(\frac{\overline{Rec}}{\sqrt{s}}\right) \quad (10)$$

Where: $\overline{Rec}$ = Recovery average and s = Standard deviation of the recovery.

In this work data from the spikes analysed in 2013 and 2014 applying this method were used to estimate the recovery of the method.

1.8. *Combined and Expanded Uncertainties*

The standard uncertainties were combined using the equation 11.

$$\mu(Conc_{Am}) = \left[\sqrt{\left(\frac{\mu V}{V}\right)^2 + \left(\frac{\mu PX}{100}\right)^2 + \left(\frac{\mu C_X}{Cx}\right)^2 + \left(\frac{\mu Repe}{100}\right)^2 + \left(\frac{\mu Rec}{100}\right)^2}\right] . C_S \quad (11)$$

Where: C_S = Concentration of the element in the sample.

To obtain the result of the expanded uncertainty, the results of combined uncertainty have to be multiplied by the expansion factor (k), to results with 95% of confidence interval k = 2.

4. RESULTS & DISCUSSION

Using the calculations described above the measurement uncertainty was estimated. Results of each source of uncertainty, combined uncertainty and expanded uncertainty are presented in TAB 1. The uncertainty source that contributes the most to all expanded uncertainties is the recovery. However, as was considered a study of 2 years to this source, the results can be considered more conservative and comprehensive. .

TABLE 1: Results of standard, combined and expanded uncertainty in the studied method.

	μ (x)/x							Expanded Uncertainty	
	V	Prep.	C_o	Rep	Rec	C_o (mg.L^{-1})	μ comb. (mg.L^{-1})	U (mg.L^{-1})	U (%)
B	0.00122	0.00792	0.01200	0.00463	0.03014	0.2499	0.0084	0.0169	6.75
Sn	0.00122	0.00847	0.01116	0.00701	0.03181	1.5230	0.0540	0.1081	7.10
Cd	0.00122	0.00803	0.00792	0.00726	0.02756	0.1260	0.0039	0.0077	6.13
Ba	0.00122	0.00893	0.00875	0.00378	0.01888	2.9710	0.0683	0.1366	4.60
Cr	0.00122	0.00851	0.01603	0.01844	0.02713	0.8110	0.0304	0.0608	7.50
Cu	0.00122	0.00807	0.00869	0.00705	0.02975	0.9210	0.0302	0.0604	6.56
Fe	0.00122	0.00841	0.00621	0.00492	0.06001	3.0610	0.1871	0.3742	12.23
Mn	0.00122	0.00794	0.01101	0.00391	0.02226	0.2725	0.0072	0.0144	5.28
Ni	0.00122	0.00892	0.00391	0.00385	0.02605	0.2555	0.0072	0.0144	5.62
Pb	0.00122	0.00807	0.01425	0.01077	0.04630	0.7720	0.0388	0.0776	10.06
Zn	0.00122	0.00839	0.00617	0.00170	0.03210	0.3243	0.0110	0.0219	6.76

5. CONCLUSÃO

Evaluating the results is possible to conclude that using data from validation process, EURACHEM guide [1] and the analyst knowledge was possible to estimate, firstly, the sources of uncertainty involved in the determination of metals in wastewater, and the expanded uncertainty of each element.

The uncertainty measured is in between 4.6% and 12.2% of the concentration determined, what is coherent with the method used.

REFERENCES

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