Uncertainty estimation in the determination of metals in superficial water by ICP-OES

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Uncertainty estimation in the determination of metals in superficial water by ICP-OES

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Abstract. From validation studies, it was possible to estimate a measurement uncertainty of several elements such as Al, Ba, Ca, Cu, Cr, Cd, Fe, Mg, Mn, Ni and K in water samples from Guarapiranga Dam. These elements were analyzed by optical emission spectrometry with inductively coupled plasma (ICP-OES). The value of relative estimated uncertainties were between 3% and 15%. The greatest uncertainty contributions were analytical curve, and the recovery method, which were related with elements concentrations and the equipment response. Water samples analyzed were compared with CONAMA Resolution #357/2005.

1. Introduction

The uncertainty of measurement according to VIM (2012), are all "*non-negative parameter that characterizes the dispersion of values of a measurand, based on the information used*" [1]. According to GUM (Guide to the Expression of Uncertainty in Measurement, 2008), the uncertainty of the result of a measurement reflects the lack of exact knowledge of the value of the measurand. Whereof the correction of recognized systematic effects, the result of measurement is only an estimation of the measurand value, originating from the random effects and imperfect correction of the results for systematic effects [2].

The result of a measurement after correction may be too close to the value of the measurand, and yet, have a negligible error, although it may have a large uncertainty. Therefore, should not confuse the uncertainty of the measurement result with the remaining unknown error occurred [2].

The EURACHEM/CITAC (2012) guide summarizes in four steps how the uncertainty estimation should be executed:

Step 1 – Specify measurand: declare clearly, what is being measured, with the inclusion of measuring and its input quantities, of which it depends;

Step 2 – Identify uncertainty sources: the inclusion of sources that will contribute to the uncertainty of the parameters in relation to Step 1, but may include other sources and also include sources resulting from chemical assumption;

Step 3 – Quantify uncertainty components: measure or estimate the size of the uncertainty component associated with each potential source of uncertainty identified;

Step 4 – Calculate combined uncertainty: with the information obtained in step 3 will contribute to the quantification of total uncertainty, whether associated with individual sources or with the combined effects of several sources. Contributions must be expressed as standard deviations, and combined

according to the appropriate rules for the combined standard uncertainty. The appropriate coverage factor should be applied to achieve an expanded uncertainty [3].

When issuing a result, it is necessary the use of a measurement uncertainty, an example, the CONAMA's Resolution 357/2005, demands that the results should be statistically analyzed taking into consideration the necessary measurement uncertainties [4]. In Table 1 shows the permissible maximum values of the analyzed elements in this work in the CONAMA's Resolution.

Table 1. Permissible Maximum Values of the analyzed elements in the CONAMA's Resolution.

Chemical Elements	CLASSE 1 Fresh Water Permissible Maximum Values (mg.L^{-1})
Dissolved Aluminum	0.1
Barium	0.7
Cadmium	0.001
Dissolved Copper	0.009
Chromium	0.05
Dissolved Iron	0.3
Manganese	0.1
Nickel	0.025
Potassium*	-
Calcium*	-
Magnesium*	-

*There is not permissible maximum concentration in CONAMA's Resolution [4].

Uncertainties were applied in the concentration results from Guarapiranga Dam's water samples. The selection of the water collection points in Guarapiranga Dam was aiming the influence of its tributaries and sub-basins in water quality. The selection was carried out with the participation of representatives of the Botanical Institute - SP, Energy and Nuclear Research Institute (IPEN) and the Center for Integration and Coordination of Information Management Environmental Planning Department of the Environment (SMA), they selected 14 points [5]. Fourteen collection points are shown in Figure 1.

Water samples were collected on 07 and 09 October 2014. The collection and sampling procedures were performed according to the procedures described in "National Guide Collection and Sample Preservation" of the National Water Agency (ANA) / Environmental Company the State of São Paulo [6] and Standard Methods for the Examination of Water and Wastewater [7].

This work intends to explain the steps of the uncertainty estimation applied to water samples collected in Guarapiranga Dam and compare to the CONAMA's Resolution 357/2015.
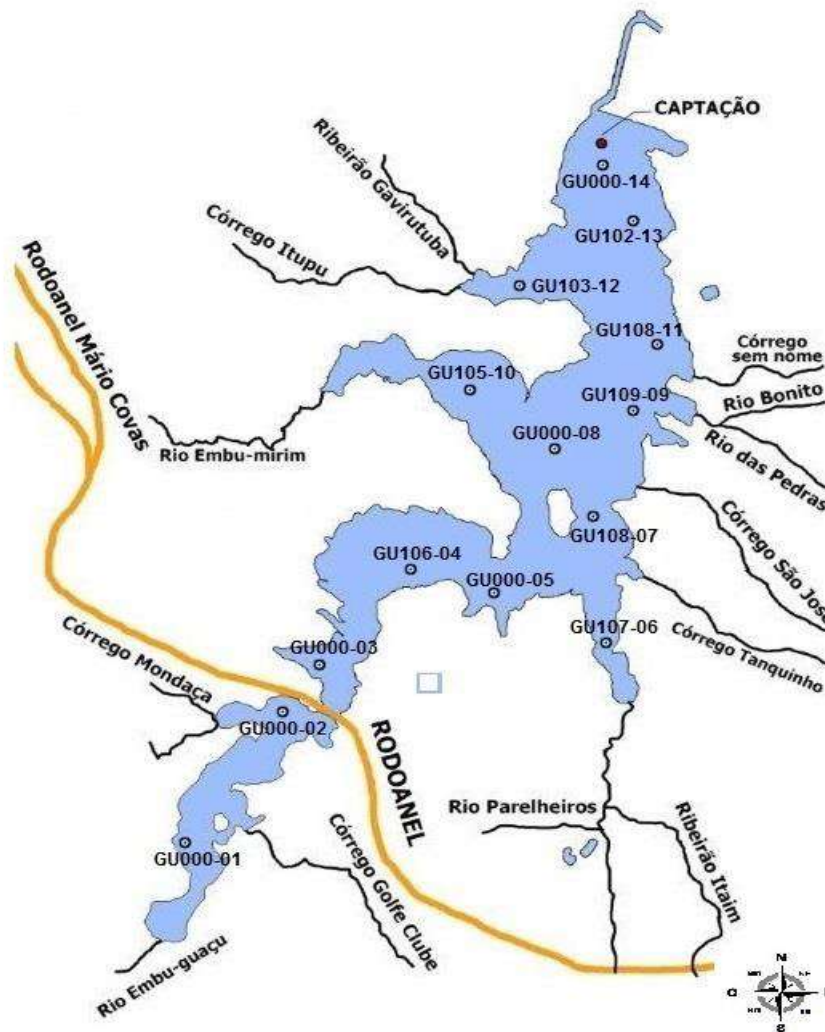
Figure 1. Distribution of collection points in Guarapiranga Dam and its tributaries [5].

2. Material and methods

Data from method development and validation of metal analysis in water was used, as follows the Ishikawa diagram (Figure 2). Uncertainties from sample and standards volume measurement, analytical curve preparation, measurement and linear regression, precision (repeatability) and recovery were estimated.

The mathematical model used to quantify the measurand is presented in (1), shows the variable that can influence the measurement of the concentration of metals in water.

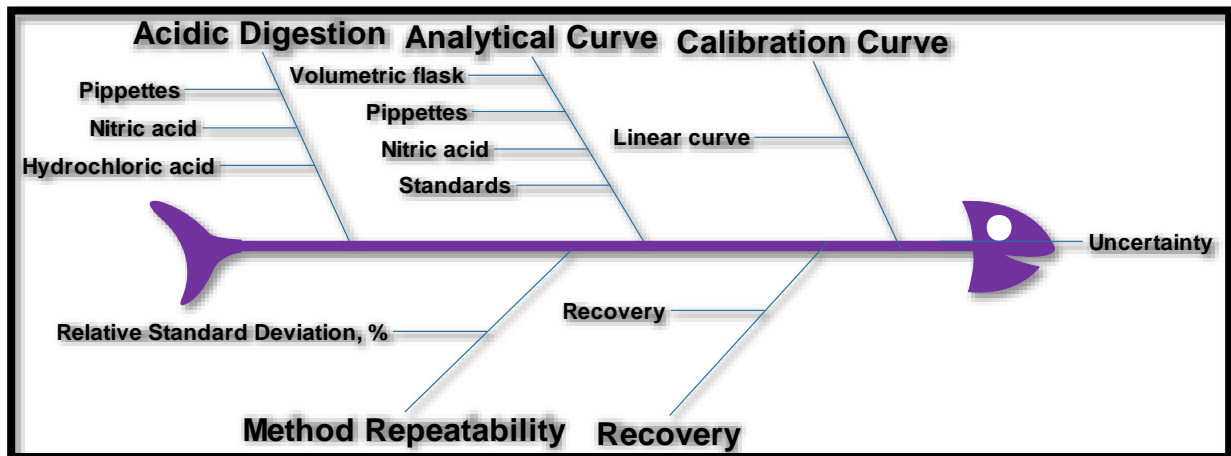$$C = \frac{C_O \text{ x } V_f}{V_i} \text{ x } \frac{1}{R} \tag{1}$$

Figure 2. Ishikawa Diagram considered for metal determination in natural waters by ICP-OES.

Where C = element concentration, mg.L^{-1}; C_O = element concentration according to analytical curve, mg.L^{-1}; V_f = final volume of the sample after digestion, 50 mL; V_i = initial volume of sample, 45 mL; R = recovery from the method [3] [5].

2.1 Uncertainty associated with acidic digestion.
The sources of uncertainty due digestion in microwave were: temperature, sample, nitric and hydrochloric acid volumes (25 mL, 4mL and 1 mL, respectively), besides pipettes repeatability used in volume measurement.

The pipettes uncertainties estimation according the sample temperature and acid collection are present in (2) [3].

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

Where $\mu(V_t)$ = uncertainty volume pipette according to temperature, mL; Q = expansion coefficient, ºC; Δ= temperature variation, ºC; V = collected volume of sample/acid, mL; $\sqrt{3}$ = rectangular distribution.
To estimate sample volume uncertainty and the acid volume uncertainty, several sources of uncertainties were combined as presented in (3).

$$\mu(V_s/V_a) = \sqrt{\mu(V_p)^2 + \mu(V_t)^2 + \mu(V_{repe})^2} \tag{3}$$

Where $\mu(V_{s/a})$ = Sample volume Uncertainty (s) and/or volume of the acid (a), mL; $\mu(V_p)$ = uncertainty of volume measurement in function of variations of Glassmaking and / or micropipette, mL; $\mu(V_{repe})$ = uuncertainty volume according repeatability, ml;
To estimate the volume combined uncertainty due acid digestion in microwave, it was used the equation (4).

$$\mu(V_f) = \sqrt{\mu(V_s)^2 + \mu(V_a)^2} \tag{4}$$

Where $\mu(V_f)$ = combined volume uncertainty due acid digestion, mL.

2.2 Uncertainty estimation on analytical curve

Uncertainties sources of analytical curve were considered as: Volume from volumetric flask and pipettes used to prepare secondary standards, nitric acid volume measurement and pipette repeatability. The uncertainty estimation was performed as presented at (5).

$$\mu(C_{PC}) = \left(\sqrt{\left(\frac{\mu V_p}{V_p}\right)^2 + \left(\frac{\mu V_{bv}}{V_{bv}}\right)^2 + \left(\frac{\mu C_{SE}}{C_{SE}}\right)^2} \right) x \; C_{PC} \tag{5}$$

Where $\mu(C_{PC})$ = Concentration uncertainty of each secondary standard of analytical curve (PC); μV_p = standard uncertainty of the pipetted volume of the SE (Stock Solution); V_p = Pipette volume of the SE, mL; μV_{bv} = uncertainty from the volumetric flask; V_{bv} = volumetric flask of volume, mL; μC_{SE} = standard uncertainty of SE; C_{SE} = elements concentration in the SE; C_{PC} = final concentration of the element on the spot.

2.3 Uncertainty associated with the calibration curve

The uncertainty estimation due to analytical curve, μ(C$_o$), was performed using the intensity data of each element measurement. [3] [5]. An example of the analytical curve used from aluminum (Al) is present in Figure 3. For calculation was used (6).

$$\mu C_0 = \frac{S}{B_1} \left(\sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(C_0 - \bar{C})^2}{S_{xx}}} \right) \tag{6}$$

Where μ(C_O) = Standard uncertainty of the analytical curve at the point 0, mg.L^{-1}; S = residual standard deviation; B_1 = slope; p = number of replicate to determine Co; n = total number of sample; C_O = sample concentration; $\bar{C}$ = average concentration of the analytical calibration curve; S_{XX} = $\sum_{i=1}^{n}(C_i - \bar{C})^2$, where Ci = concentration value obtained from the calibration curve.
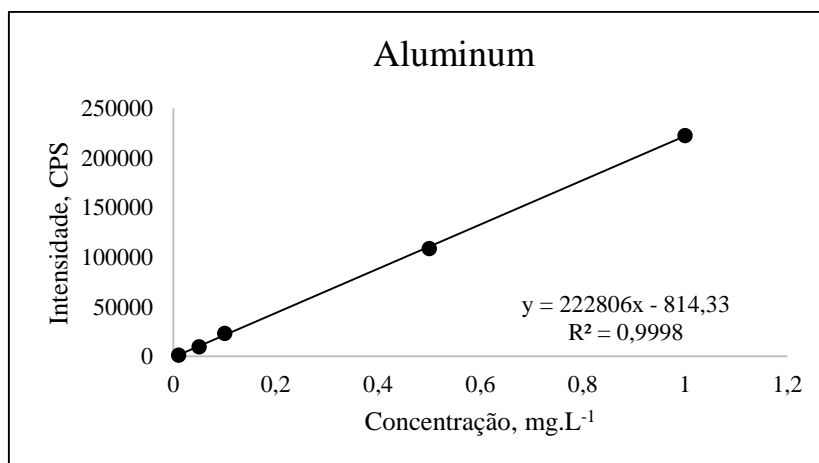

Figure 3. Al Analytical curve.

2.4 Method Repeatability Uncertainty

To estimate the uncertainty due method repeatability, it was used the relative standard deviation (RSD%) of the samples with standard addition measurement of the analytical curve intermediate point each studied element. For the calculation, was used (7).

$$\mu(Repe) = \left(\frac{Máx\ DPR}{\sqrt{n}} \right) \tag{7}$$

Where $Máx\ DPR$ = Higher deviation of replicate values; n = number of replicates.

2.5 Recovery Uncertainty

The recovery uncertainty was obtained from recovery tests performed on method validation, in which standard additions were made in seven independent samples in ten replicates for each element. Thereafter was the average of the replicates used for calculating the measurement uncertainty associated recovery according to (8).

$$\mu(Rec) = \left(\frac{\overline{Rec}}{\sqrt{s}} \right) \tag{8}$$

Where $\overline{Rec}$ = average method of recovery for the element; s = standard deviation of recovery.

2.6 Combined and expanded uncertainty

As step 4 of the EURACHEM/CITAC (2012) guide was performed combining all sources of uncertainty using (9).

$$\mu(C_s) = \left(\sqrt{ \left(\frac{\mu V}{V}\right)^2 + \left(\frac{\mu C_{PC}}{C_{PC}}\right)^2 + \left(\frac{\mu C_O}{C_o}\right)^2 + \left(\frac{\mu Repe}{Rep}\right)^2 + \left(\frac{\mu Rec}{Rec}\right)^2 } \right) x\ C_s \tag{9}$$

Where μV_f = standard uncertainty of volume, mL; V_f = total volume, mL; μC_{PC} = higher standard uncertainty of the points in the calibration curve, %; μC_O = standard uncertainty adjusting the calibration curve, mg.L^{-1}; Co = concentration of a point of the calibration curve, mg.L^{-1}; $\mu Repe$ = standard uncertainty of repeatability, %; μRec = standard uncertainty of recovery, %; C_s = sample concentration, mg.L^{-1}.

The relative extended uncertainty estimation was performed using an expansion factor of uncertainty k = 2, using a 95% confidence interval of the results obtained, presented in (10).

$$U = \mu(C_s)\ x\ k \tag{10}$$

Where U = relative expanded uncertainty; $\mu(C_s)$ = final uncertainty of the concentration of the sample; k = expansion factor = 2

3. Results and Discussion

As an example, Aluminum expanded relative uncertainty estimation (%) was 12% and are presented in Table 2. The other elements such as Ba, Ca, Cd, Cu, Cr, Fe, K, Mg, Mn, e Ni, presented values of 3%, 3%, 5%, 13%, 4%, 5%, 15%, 8%, 4%, and 4%, respectively.

Aluminum (Al), Ba, Ca, Cd, Cu, Fe, K, Mg, Mn and Ni showed high values of contributions to the uncertainty associated with analytical curve μ (Co), as they relate to the analyte concentration and instrument response. Some elements, such as Cu, K and Al showed high values in uncertainty associated with recovery μ (Rec) as equal to analytical curve element is related to the concentration in the sample and may have variations in concentration. Samples from Guarapiranga Dam were analyzed by ICP-OES. Data are presented in Table 3.

Table 2. Uncertainties components used to estimate Aluminum expanded uncertainty.

Source	Value (x)	$\mu(x)$	$\mu(x)/x$
$\mu(V_f)$, mL	50	0.061	0.00122
$\mu(C_{PC})$, %	100	1.421	0.01421
$\mu(C_o)$, mg.L^{-1}	0.098	0.003	0.02670
$\mu(Rep)$, %	100	0.017	0.00017
$\mu(Rec)$, %	98	5.194	0.05300
$\mu(C_s)$		0.006	
U (k=2)		0.012	

Table 3. Elements concentration with the uncertainty (mg.L^{-1}).

Collection points	Mg	K	Ca	Al	Cr	Mn	Fe	Ni	Cu	Cd	Ba
G000-01 S	0.61 ±0.05	1.49 ±0.22	1.70 ±0.04	0.23 ±0.014	<LQ	0.044 ±0.002	1.23 ±0.06	<LQ	<LQ	<LQ	<LQ
G000-02 S	0.74 ±0.06	1.82 ±0.27	2.47 ±0.06	0.28 ±0.017	<LQ	0.037 ±0.002	1.12 ±0.05	<LQ	<LQ	<LQ	<LD
G000-03 S	0.92 ±0.07	2.37 ±0.35	3.78 ±0.10	0.16 ±0.010	<LQ	0.029 ±0.001	0.45 ±0.02	<LQ	<LQ	<LQ	LD
G000-04 S	1.16 ±0.09	2.96 ±0.44	5.49 ±0.14	0.10 ±0.006	<LQ	0.039 ±0.002	0.21 ±0.01	<LQ	<LQ	<LQ	<LQ
G000-05 S	1.56 ±0.12	3.83 ±0.57	8.20 ±0.21	0.04 ±0.003	<LQ	0.075 ±0.003	0.17 ±0.01	<LQ	0.024 ±0.003	<LQ	<LQ
G107-06 S	1.68 ±0.13	4.13 ±0.62	9.28 ±0.24	0.09 ±0.006	<LQ	0.092 ±0.004	0.29 ±0.01	<LQ	0.023 ±0.003	<LQ	<LQ
G108-07 S	1.61 ±0.12	4.02 ±0.60	8.64 ±0.22	0.058 ±0.004	<LQ	0.094 ±0.004	0.19 ±0.01	<LQ	0.032 ±0.004	<LQ	<LQ
G000-08 S	1.63 ±0.13	4.01 ±0.60	8.75 ±0.23	0.044 ±0.003	<LQ	0.072 ±0.003	0.12 ±0.01	<LQ	0.026 ±0.003	<LQ	0.012 ±0.032
G109-09 S	1.61 ±0.12	4.02 ±0.60	8.70 ±0.22	0.043 ±0.003	<LQ	0.072 ±0.003	0.13 ±0.01	<LQ	0.021 ±0.003	<LQ	<LQ
G105-10 S	1.73 ±0.13	4.32 ±0.64	9.14 ±0.23	0.08 ±0.003	<LQ	0.081 ±0.003	0.24 ±0.01	<LQ	0.016 ±0.002	<LQ	0.01 ±0.03
G104-11 S	1.68 ±0.13	4.20 ±0.61	9.01 ±0.23	0.10 ±0.002	<LQ	0.047 ±0.002	<LQ	<LQ	0.038 ±0.005	<LQ	<LQ
G103-12 S	1.64 ±0.13	4.23 ±0.63	8.78 ±0.23	0.016 ±0.002	<LQ	0.055 ±0.002	0.17 ±0.01	<LQ	0.035 ±0.005	<LQ	0.01 ±0.03
G102-13 S	1.60 ±0.12	4.06 ±0.61	8.50 ±0.22	0.062 ±0.002	<LQ	0.046 ±0.002	<LQ	<LQ	0.039 ±0.005	<LQ	<LQ
G000-14 S	1.59 ±0.12	4.03 ±0.60	8.52 ±0.22	0.25 ±0.002	<LQ	0.050 ±0.002	0.13 ±0.01	<LQ	0.041 ±0.005	<LQ	<LQ

Elements such as Fe, Al and Cu showed values above CONAMA Resolution 357/2005. Fe is related to geological characteristic of the area; Al in some points is associated with aluminum sulfate also used as flocculant in the dam, in water treatment, once Guarapiranga is used as one main source of water public supply; and Cu is used as copper sulfate, to prevent algae blooms that are frequent in the region.

Other evaluated elements such as Cd, Cr Ba, Mn, Mg, K and Ni are present below permitted values by Brazilian regulation and were considered satisfactory.

4. Conclusion
By using method development and validation procedures it was possible to identify the most significant uncertainties sources and with EURACHEM/CITAC guide (2012) it was possible to estimate expanded uncertainties of all elements measures in water samples collected at Guarapiranga Dam and compare its values with appropriated regulation.

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