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Validation and uncertainty estimation for multielement determination using ICP-OES according to the ASTM E2941-14 standard

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Abstract: Standardized analytical methods for determining elemental concentrations require thorough validation and estimation of measurement uncertainty. Inductively coupled plasma optical emission spectrometry (ICP-OES) is a widely used technique for multielement analysis with the ASTM E2941-14 standard specifying the analytical conditions for its application. This study aims to validate the ICP-OES method and estimate the expanded uncertainty for multielement determination in accordance with ASTM E2941-14. Method validation and uncertainty estimation were conducted following Eurachem (2014) and Eurachem-CITAC (2012) guidelines, respectively. The method demonstrated acceptable linearity, with coefficients of determination (R^2) ranging from 0.9972 to 1.0000 and correlation coefficients (R) from 0.9982 to 1.0000, exceeding the acceptance criterion ($R^2/R \geq 0.995$). Accuracy under repeatability conditions showed coefficients of variation between 1.0% and 8.0%, indicating good consistency. Trueness evaluation revealed no significant bias, with recovery rates within the acceptable range of 100% ± 10%. Combined uncertainty values ranged from 0.0425 (silver; Ag) to 0.5156 (scandium; Sc), corresponding to relative uncertainties of 1.25% to 8.16%, respectively. Expanded uncertainties ranged from 0.0850 (Ag) to 1.0312 (Sc). The dominant sources of relative uncertainty were associated with calibration curve-based concentration measurements and volumetric equipment.

Keywords: Validation; sources of uncertainty; expanded uncertainty; ASTM E2941-14; ICP-OES.

1. Introduction

A wide array of analytical techniques is available for the determination of chemical elements in both organic and inorganic matrices [1–3]. The selection of a suitable method depends on the specific analytical objectives and the capabilities of the laboratory. Mono-elemental techniques such as flame atomic absorption spectroscopy and electrothermal atomic absorption spectroscopy are commonly used, enabling the quantification of approximately 70 elements [4–6]. However, inductively coupled plasma optical emission spectrometry (ICP-OES) has emerged as one of the most versatile and efficient techniques [7–9], allowing for the simultaneous determination of multiple elements with high sensitivity and throughput [10–12]. The use of certified reference materials is critical in ensuring the reliability and

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traceability of analytical results across all methodologies [13–18]. These materials provide a benchmark that supports the accuracy of measurements and helps validate method performance. In this context, method validation and uncertainty estimation are essential components of quality assurance, particularly for laboratories engaged in accreditation and certification processes. Compliance with international standards, such as ISO/IEC 17025:2017, is necessary to demonstrate the competence and reliability of analytical results, including those generated by qualified personnel [19–21]. Furthermore, the ASTM E2941-14 standard outlines procedures for the extraction and determination of a wide range of elements—including aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), bismuth (Bi), boron (B), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), gallium (Ga), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), phosphorus (P), potassium (K), scandium (Sc), selenium (Se), silver (Ag), sodium (Na), strontium (Sr), thallium (Tl), tin (Sn), titanium (Ti), vanadium (V), and zinc (Zn)—from minerals and related metallurgical materials. These elements are quantified in solution using analytical techniques such as ICP-OES [22–24]. ASTM E2941-14 is closely aligned with other relevant standards, including ASTM D1976-20, D5673-16, and E882-10(2016)e1. Notably, ASTM E882 emphasizes the importance of robust laboratory management systems that ensure accountability and quality control. It states, "Laboratory management must implement a system of accountability and quality control to enhance the reliability of its results. This system generates documented records that reassure laboratory clients that a defined level of accuracy is consistently achieved in routine measurements and that the reported data originate from the submitted samples". This study aimed to validate and estimate the expanded uncertainty associated with multielement determination using ICP-OES, thereby enhancing the accuracy and reliability of elemental analysis. This objective was achieved by ensuring measurement traceability and quality through the use of certified reference materials, following the sample digestion procedure specified in ASTM E2941-14. The multielement approach not only improves analytical efficiency but also provides a rigorous framework for uncertainty estimation—an essential requirement for compliance with international quality standards in chemical metrology and laboratory accreditation. Moreover, in industrial applications, this methodology enhances the reliability of detecting trace-level contaminants or elements due to the high sensitivity of ICP-OES. Compared to other analytical techniques, ICP-OES offers significant advantages, including simultaneous multielement analysis, reduced sample preparation, and increased analytical throughput, making it a preferred choice in high-demand laboratory environments.

2. Experimental

2.1. Materials and Methods

2.1.1. Reference Materials

The following certified reference materials (CRMs) were used for calibration and quality control purposes: ICP-MS-68B-A250 (matrix: 4% HNO_3; purity: 99.96%–99.9999%; lot number 2404609-250; manufacturer: High-Purity Standards), ICP-MS-68B-B-500 (matrix: 2% HNO_3/Tr HF; purity: 99.2%–99.999%; lot number 2308110-500; manufacturer: High-Purity Standards), and sulfur 100054-5-250 (matrix: H_2O; lot number 2106313-250; manufacturer: High-Purity Standards).

2.1.2. Reagents

Analytical-grade reagents were used throughout the study; hydrochloric acid (HCl; purity: 37.3%; lot number: 946142; manufacturer: Productos Químicos Monterrey S.A. de C.V.), hydrofluoric acid (HF; purity: 40.8%; lot number: B1895538; manufacturer: Merck KGaA), nitric acid (HNO_3; purity: 65.3%; lot number: K49640256; manufacturer: Merck KGaA), perchloric acid ($HClO_4$; purity: 70%–72%; lot number: B1836319; manufacturer: Merck KGaA), and triple-distilled water (19 L container; lot number: 449787; catalog number: 6541; manufacturer: Hycel Reactivos Químicos).

2.1.3. Sample Digestion

A 0.2000-g portion of each sample was accurately weighed into a PTFE digestion beaker. Subsequently, 10 mL of a multi-acid mixture comprising HF, HNO_3, HCl, $HClO_4$, and H_2O and distilled water was added. The mixture was digested on a LabTech hot plate (models EG20B and EG35B) at a temperature range of 70°C–75 °C until complete dryness was achieved. After digestion, the residue was treated with 100 mL of hydrochloric acid, and the final solution was diluted to volume using triple-distilled water in a 50 mL Pyrex Class A volumetric flask.

2.1.4 Instrumentation and Operating Conditions

Elemental analysis was conducted using an Agilent 5110 inductively coupled plasma optical emission spectrometer, serial number MY18250004. The instrument was operated according to the manufacturer’s specifications and configured for optimal multielement detection.

2.2 Analytical Method Validation

The analytical procedure for multielement determination by ICP-OES was validated by evaluating linearity, limits of detection (LOD) and quantification (LOQ), accuracy, and expanded measurement uncertainty. The mathematical approaches employed followed the recommendations of Magnuson and Örnemark, as outlined in the Eurachem Guide: The Fitness for Purpose of Analytical Methods (2nd ed., 2014) [25] for method validation, and were recently applied in prior work by our research group [26]. Linearity was evaluated using four calibration curves constructed at five concentration levels (0.5, 1.0, 3.0, 6.0, and 10.0 mg/L) for each of the 29 target elements. CRMs (Table 1) were used to ensure traceability. The LOD and LOQ were determined based on the standard deviation of 30 digestion blank measurements. Accuracy was assessed under repeatability conditions by analyzing replicate samples, while trueness was evaluated through bias analysis and recovery studies. Additionally, 10 replicate measurements of standards containing 3.0 mg/L of all 29 elements were performed to verify method consistency and reproducibility.

2.3 Estimation of the Expanded Uncertainty of the Analytical Method

The estimation of standard, relative, combined, and expanded uncertainties (with a coverage factor $\kappa = 2$) followed the methodology recommended by Ellison and Williams in the Eurachem/CITAC Guide CG4: Quantifying Uncertainty in Analytical Measurement (2012) [27], as recently adopted in related work by our research group [26].

Uncertainty estimation considered contributions from multiple sources, including the concentration values obtained from calibration curves, tolerances associated with volumetric equipment, dilution factors, the precision of the analytical balance, repeatability under defined conditions, and the uncertainties linked to CRMs. Relative uncertainties were quantified and used to assess the contribution of each source to the overall combined uncertainty. These contributions are graphically represented in the Ishikawa diagram shown in Figure 1, which summarizes the primary uncertainty sources evaluated in this study.

Table 1. Certified reference materials used in the ICP-OES method validation process according to ASTM E2941-14.

CRM	Element	mg/mL +/- Uncertainty	SRM ID	Lot number
ICP MS-68B-A250	Al	100 +/- 0.6	3101a	1919318-250
	As	100 +/- 1.0	3103a	
	Ba	100 +/- 0.6	3104a	
	Be	100 +/- 1.0	3105a	
	Bi	100 +/- 1.0	*	
	Ca	100 +/- 0.6	3109a	
	Cd	100 +/- 0.6	3108	
	Co	100 +/- 0.6	*	
	Cu	100 +/- 0.6	3114	
	Fe	100 +/- 0.6	3126a	
	K	100 +/- 1.0	3141a	
	La	100 +/- 0.6	3127a	
	Li	100 +/- 1.0	3129a	
	Mg	100 +/- 0.6	3131a	
	Mn	100 +/- 1.5	*	
	Na	100 +/- 0.6	3152a	
	Ni	100 +/- 0.6	3136	
	P	100 +/- 1.5	3139a	
	Pb	100+/-1.0	3128	
	Sc	100+/-1.0	3148a	
	Sr	100 +/- 0.6	*	
	U	100 +/- 0.6	3164	
	V	100+/-1.0	3165	
ICP MS -68-B-250	Ag	100+/-1.0	3151	1929532-250
	Mo	100+/-1.0	3134	
	Sb	100+/-1.0	3102a	
	Sn	100+/-1.0	3161a	
AQ0-132-291	S	100+/- 0.8	3162 a	S200107-021
	W	100+/-1.0		
ICP MS-1-250	Zn	100 +/- 0.6	3168a	1911421-250

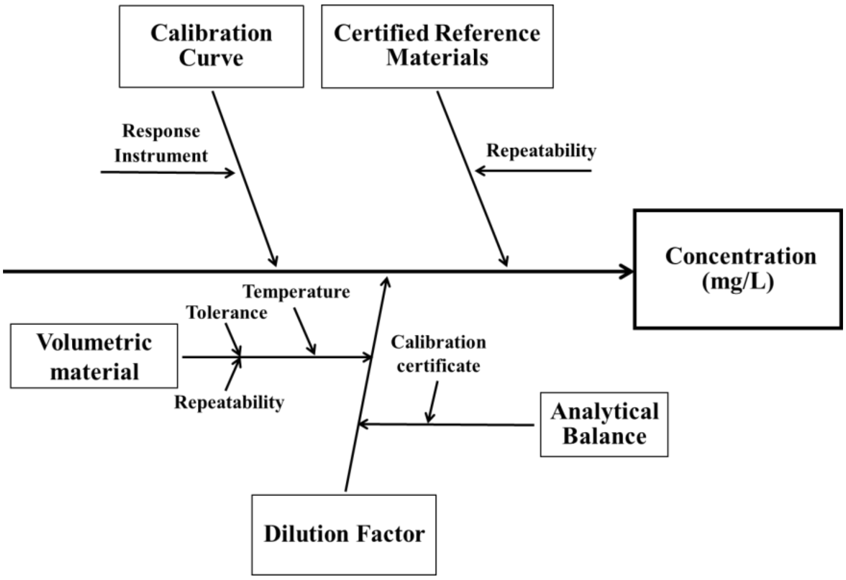

Figure 1. Ishikawa model showing the sources of uncertainty considered in this research.

3. Results and Discussion

3.1. Results

3.1.1. Validation: Aluminum as an Example

3.1.1.1. Linearity

To illustrate the validation procedure, Al was selected as a representative example. The calibration curve was constructed by plotting the concentration of Al on the x-axis against the corresponding average emission intensity on the y-axis, as shown in Table 2. A linear regression analysis yielded the calibration equation and the coefficient of determination (R^2 or r^2). The Pearson correlation coefficient (R) was obtained by taking the square root of R^2. The graphical results are provided in Figure 1. As shown in Figure 2, the calibration curve for Al resulted in $R^2 = 0.9994$ and $R = 0.9997$, indicating excellent linearity. This procedure was applied consistently across all other analytes, with their corresponding results summarized in Table 3. The linearity results meet the established acceptance criterion for chemical measurements, which requires $R^2/R \geq 0.995$ [25].

Table 2. Four calibration curves for aluminum using five concentration points analyzed by ICP-OES.

Al concentration [mg/L]	Intensity 1	Intensity 2	Intensity 3	Intensity 4	Mean
0.5	11764.96000	11867.65900	11905.07200	11825.72900	11840.85500
1	23270.85800	23368.06400	23660.88700	23054.11200	23338.48025
3	73114.77600	72768.48500	72208.19700	71405.45900	72374.22925
6	150015.39800	149114.68400	151949.42700	146789.32700	149467.20900
10	259867.06700	256542.54300	263246.05500	253751.64400	258351.82725

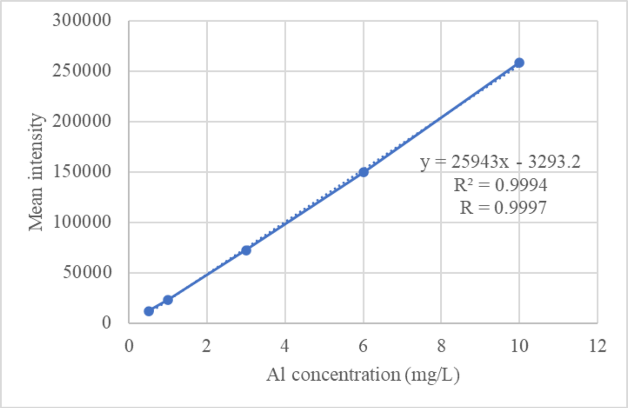

Figure 2. Calibration curve for aluminum. R^2 and R represent the coefficient of determination and Pearson correlation coefficient, respectively.

Table 3. Determination of the regression coefficient (R^2) and Pearson correlation coefficient (R) values obtained from the calibration curves for each of the chemical elements evaluated.

Element	R^2	R
Ag	1.0000	1.0000
As	0.9998	0.9999
Be	0.9972	0.9982
Bi	1.0000	1.0000
Ca	0.9999	0.9999
Cd	0.9992	0.9996
Co	1.0000	1.0000
Cu	0.9998	0.9999
Fe	0.9999	0.9999
K	0.9999	0.9999
La	0.9999	0.9999
Li	0.9997	0.9998
Na	0.9983	0.9991
Mg	0.9997	0.9998
Mn	0.9997	0.9998
Mo	1.0000	1.0000
Ni	0.9999	0.9999
P	0.9999	0.9999
Pb	0.9995	0.9997
S	0.9997	0.9998
Sb	1.0000	1.0000
Sc	0.9999	0.9999
Sn	0.9999	0.9999
Sr	0.9990	0.9995
U	1.0000	1.0000
Va	1.0000	1.0000
W	1.0000	1.0000
Zn	0.9993	0.9996

3.1.1.2. LOD and LOQ

LOD and LOQ were determined using a reagent blank containing the same four acids employed in the digestion procedure but excluding the target analytes. The blank was measured 10 times under identical instrumental conditions, and the mean signal and standard deviation ($\sigma = 0.024$) were calculated. These values were then applied to standard formulas to calculate LOD and LOQ.

Aluminum is presented as an illustrative example in this section, while the same approach was used for the remaining elements, with their corresponding results provided in Table 4.

$$Sd' = 0.024/\sqrt{10} = 0.007$$
$$LOD = 3*0.007 = 0.023 \text{ mg/L}$$
$$LOQ = 10*0.007 = 0.070 \text{ mg/L}$$

Table 4. LOD and LOQ for the other 28 chemical elements (CE)

CE	MEAN	SD	SD´	LOD	LOQ
Al	0.055	0.024	0.007	0.023	0.07
Ag	0.028	0.011	0.003	0.010	0.10
As	0.001	0.003	0.001	0.003	0.03
Be	0.000	0.044	0.014	0.041	0.41
Bi	0.004	0.000	0.000	0.000	0.00
Ca	0.980	0.006	0.002	0.006	0.06
Cd	0.001	0.006	0.000	0.001	0.01
Co	0.001	0.001	0.000	0.001	0.01
Cu	0.005	0.001	0.000	0.001	0.01
Fe	0.059	0.008	0.003	0.008	0.08
K	0.018	0.013	0.004	0.013	0.13
La	0.000	0.012	0.004	0.012	0.12
Li	0.001	0.001	0.000	0.001	0.01
Mg	0.031	0.002	0.001	0.002	0.02
Mn	0.003	0.010	0.003	0.010	0.10
Mo	0.003	0.002	0.001	0.002	0.02
Na	0.109	0.001	0.000	0.001	0.01
Ni	0.003	0.085	0.027	0.081	0.81
P	0.010	0.002	0.001	0.002	0.02
Pb	0.025	0.006	0.002	0.006	0.06
S	0.013	0.010	0.003	0.009	0.09
Sb	0.004	0.048	0.015	0.046	0.46
Sc	0.001	0.013	0.004	0.012	0.12
Sn	0.003	0.002	0.001	0.002	0.02
Sr	0.003	0.003	0.001	0.003	0.03
U	0.003	0.002	0.001	0.002	0.02
V	0.000	0.004	0.001	0.004	0.04
W	0.004	0.001	0.000	0.001	0.01
Zn	0.303	0.002	0.001	0.002	0.02

3.1.1.3. Accuracy under Repeatability Conditions

Repeatability was evaluated through the coefficient of variation (CV), calculated from replicate measurements under the same operating conditions. Aluminum is again used to exemplify the calculation (Table 5), and the same procedure was applied to all other analytes, with the full results summarized in Table 6.

Table 5. Determination of %CV to evaluate precision under repeatability conditions, for the case of Al.

Element (Al)	Intensity
Replica 1	62212.45
Replica 2	62368.32
Replica 3	62076.41
Replica 4	62649.16
Replica 5	62039.30
Replica 6	63454.54
Replica 7	63564.63
Replica 8	61536.92
Replica 9	62222.89
Replica 10	62223.36
Mean	62434.80
Standard deviation	632.18
% CV	1.01%

Table 6. Determination of %CV for precision under repeatability conditions for the remaining 28 chemical elements.

Element	% CV
Ag	2.00
As	1.00
Be	1.00
Bi	1.00
Ca	2.00
Cd	1.00
Co	1.00
Cu	1.00
Fe	8.00
K	2.00
La	1.00
Li	1.00
Mg	1.00
Mn	1.00
Mo	1.00
Na	2.00
Ni	1.00
P	1.00
Pb	4.00
S	3.00
Sb	1.00
Sc	1.00
Sn	1.00
Sr	3.00

U	1.00
V	1.00
W	1.00
Zn	5.00

3.1.1.4. Trueness through Bias and/or Recovery Percentage

Trueness was assessed by calculating the bias, defined as the difference between the mean measured concentration and the certified reference value. The calculated bias was evaluated against the Z-score threshold at a 95% confidence level to determine acceptability. Aluminum is presented as a representative example, with results shown in Table 7. Comparable findings were obtained for the other 28 elements, though detailed data are not presented here.

Table 7. Determination of bias and recovery percentage, for the case of Al.

Element (Al)	**Intensity**
Replica 1	62212.45
Replica 2	62368.32
Replica 3	62076.41
Replica 4	62649.16
Replica 5	62039.30
Replica 6	63454.54
Replica 7	63564.63
Replica 8	61536.92
Replica 9	62222.89
Replica 10	62223.36
Mean	62434.80
Standard deviation	632.18
Bias*	-2434.8
Z-score (1.96)	391.82
% Recovery	104.06

* Bias ≤ Z-score. So there is no bias, there is accuracy.

3.1.2. Uncertainty: Aluminum as an Example

The combined uncertainty associated with volumetric equipment was calculated by quadratically summing the individual uncertainties arising from instrument tolerance, repeatability, and temperature variation for each volumetric device used.

Figure 3 presents the relative contribution of the main sources of uncertainty influencing the measurement method. As shown, the most significant contributors to the uncertainty in Al determination were the concentration derived from the calibration curves and the volumetric equipment. A similar trend was observed across the remaining 28 chemical elements evaluated in this study.

3.1.2.1. Uncertainty of the Concentration from the Calibration Curves

3.1.2.1.2. Standard Uncertainty

$$u_{y_x} = \frac{3650.99}{25943} * \sqrt{\frac{1}{5} + \frac{1}{20} + \frac{\left(4.3\dot{5}38 - 4.\dot{1}\right)^2}{62.20}} = 0.060\ \mu\text{g/mL}$$

3.1.2.1.3 Relative Uncertainty

$$u_{r_{y_x}} = \sqrt{\left(\frac{0.060}{3}\right)^2} = 0.02$$

Table 8 shows the standard and relative uncertainty results for concentration from calibration curves for the remaining 28 chemical elements.

Table 8. Determination of standard and relative uncertainty of concentration from calibration curves for the remaining 28 chemical elements

Element	u_{y_x}	$u_{r_{y_x}}$
Ag	0.258	0.063
As	0.260	0.063
Be	0.178	0.043
Bi	0.521	0.127
Ca	0.479	0.099
Cd	0.199	0.048
Co	0.253	0.062
Cu	0.553	0.135
Fe	0.051	0.125
K	0.172	0.042
La	0.242	0.059
Li	0.067	0.016
Mg	0.652	0.159
Mn	0.170	0.041
Mo	0.230	0.056
Na	0.034	0.008
Ni	0.190	0.046
P	0.174	0.042
Pb	0.477	0.116
S	0.024	0.006
Sb	1.156	0.282
Sc	0.236	0.058
Sn	0.200	0.049
Sr	1.690	0.412
U	2.750	0.671
V	0.202	0.049
W	0.930	0.227
Zn	0.098	0.024

3.1.2.2. Uncertainty for the Volumetric Material

3.1.2.2.1. Tolerance (Tol)

For 1 mL $u_{tol} = \frac{0.025}{\sqrt{6}} = 0.010$

For 50 mL $u_{tol} = \frac{0.06}{6} = 0.024$

3.1.2.2.2 Combined Standard Uncertainty for the Tolerance

$$u_{comb\ tol} = \sqrt{(0.010)^2 + (0.024)^2} = 0.011$$

3.1.2.2.3. Combined Relative Uncertainty for the Tolerance

$$u_{r_{comb\ tol}} = \sqrt{\left(\frac{0.010}{0.025}\right)^2 + \left(\frac{0.024}{0.06}\right)^2} = 0.56$$

3.1.2.3. Repeatability (R)

For 1 mL $u_R = \frac{0.0024}{\sqrt{6}} = 0.00098$

For 50 mL $u_R = \frac{0.1085}{\sqrt{6}} = 0.044$

3.1.2.3.1. Combined standard uncertainty for the repeatability

$$u_{comb\ rep} = \sqrt{(0.00098)^2 + (0.044)^2} = 0.014$$

3.1.2.3.2. Combined relative uncertainty for the repeatability

$$u_{r\ comb\ rep} = \sqrt{\left(\frac{0.00098}{1}\right)^2 + \left(\frac{0.044}{50}\right)^2} = 0.014$$

3.1.2.4. Temperature Variation (ΔT) (28 ºC)

For 1 mL

$$u_{\Delta T} = \frac{[(28-20)\cdot 0.00021\cdot 1]}{\sqrt{3}} = 0.00048$$

For 50 mL

$$u_{\Delta T} = \frac{[(28-20)\cdot 0.00021\cdot 50]}{\sqrt{3}} = 0.02425$$

3.1.2.4.1. Combined Standard Uncertainty for the Temperature Variation

$$u_{comb\ \Delta T} = \sqrt{(0.00048)^2 + (0.02425)^2} = 0.0011$$

3.1.2.4.2. Combined Relative Uncertainty for the Temperature Variation

$$u_{r\ comb\ \Delta T} = \sqrt{\left(\frac{0.00048}{1}\right)^2 + \left(\frac{0.02425}{50}\right)^2} = 0.00068$$

To obtain the combined uncertainty due to the volumetric material, it is necessary to combine the uncertainties of tolerance, repeatability, and temperature variation in a quadratic manner for each of the volumetric materials.

3.1.2.4.3. Combined Uncertainty for the Tolerance, Repeatability and Temperature Variation

For 1 mL $$u_{comb\ vol\ mat} = \sqrt{(0.014)^2 + (0.00098)^2 + (0.00048)^2} = 0.0140$$

For 50 mL $$u_{comb\ vol\ mat} = \sqrt{(0.035)^2 + (0.04431)^2 + (0.02425)^2} = 0.0614$$

3.1.2.4.4. Combined Uncertainty for the Volumetric Material

$$u_{comb\ vol\ mat} = \sqrt{(0.0140)^2 + (0.0614)^2} = 0.0630$$

3.1.2.4.5. Combined Relative Uncertainty for the Volumetric Material

$$u_{r_{comb\ vol\ mat}} = \sqrt{\left(\frac{0.0140}{1}\right)^2 + \left(\frac{0.0614}{50}\right)^2} = 0.0140$$

3.1.3. Standard Uncertainty of Dilution Factor

$$u_{fd_n} = \sqrt{(0.0140)^2 + (0.0614)^2} = 0.0630$$

3.1.3.1. Relative Uncertainty of Dilution Factor

$$u_{fd} = \sqrt{\left(\frac{0.0630}{50}\right)^2} = 0.0013$$

3.1.4. Uncertainty of the Analytical Balance

Where the standard uncertainty of the analytical balance is obtained from the calibration certificate No. 116752 with a reported value of 0.00029 of the expanded uncertainty (*U*) for a value of k=2.

3.1.4.1. Standard Uncertainty of the Analytical Balance

$$u_{balance} = \frac{U_{certificate}}{k} = \frac{0.00029}{2} = 1.45 \times 10^{-4}$$

Table 9. Estimation of standard uncertainty and relative uncertainty for precision under repeatability conditions.

Element	Standard uncertainty	Relative uncertainty
As	0.0099	0.0031
Ba	0.0111	0.0037
Be	0.0109	0.0036
Bi	0.0098	0.0033
Ca	0.0145	0.0048
Cd	0.0093	0.0031
Cu	0.0112	0.0037
Co	0.0098	0.0033
Fe	0.0801	0.0267
K	0.0171	0.0057
La	0.0097	0.0032
Li	0.0105	0.0035
Mg	0.0132	0.0044
Mn	0.0108	0.0036
Na	0.0218	0.0073
Ni	0.0124	0.0041
P	0.0118	0.0039
Pb	0.0364	0.0121
Sc	0.0107	0.0036
Sr	0.0291	0.0097
U	0.0109	0.0036
Va	0.0096	0.0032
Ag	0.0206	0.0069
Mo	0.0067	0.0022
Sb	0.0056	0.0019
Sn	0.0080	0.0027
S	0.0267	0.0089
W	0.0059	0.0019
Zn	0.0523	0.0174

3.1.4.2. Relative Uncertainty of the Analytical Balance (mass = 30 mg)

$$u_{r\ balance} = \frac{u_{balance}}{m} = \frac{0.000145}{30} = 4.83 \text{ x } 10^{-6}$$

3.1.5 Uncertainty for the Precision under Repeatability Conditions

Example: Aluminum.

A 3 mg/L standard was used with 10 replicates. The mean value was 3.0114 mg/L with a standard deviation of 0.037.

3.1.5.1. Standard Uncertainty for the Precision Under Repeatability Conditions

$$\sqrt{\left(\frac{0.037}{\sqrt{10}}\right)^2} = 0.0117$$

3.1.5.2. Relative Uncertainty for the Precision Under Repeatability Conditions

$$\sqrt{\left(\frac{0.0117}{3}\right)^2} = 0.0039$$

Similarly, the standard and relative uncertainty for the precision under repeatability conditions was obtained for the remaining 28 chemical elements evaluated. These values are presented in Table 9.

3.1.6. Uncertainty for the Certified Reference Material

The uncertainty of the mass concentration of the NIST-traceable CRM for aluminum is reported by the producer of the reference material. It is necessary to divide the uncertainty by the coverage factor k=2. A rectangular distribution is assumed. The concentration of aluminum is 100 mg/L.

3.1.6.1. Standard Uncertainty for the Certified Reference Material

$$u_{CRM} = \frac{U_{certificate}}{k} = \frac{0.6}{2} = 0.3$$

$$u_{CRM} = \frac{u_{CRM}}{\sqrt{3}} = = \frac{0.3}{\sqrt{3}} = 0.1732$$

3.1.6.2. Relative Uncertainty for the Certified Reference Material

$$u_{r\ CRM} = \sqrt{\left(\frac{0.1732}{100}\right)^2} = 0.00173$$

Similarly, the standard and relative uncertainty for the CRM of the remaining 28 chemical elements evaluated were obtained. These values are presented in Table 10.

3.1.7. Combined Uncertainty for All the Sources of Uncertainty

The standard uncertainties of the concentration from the calibration curve, the volumetric material, the dilution factor, the analytical balance, the precision under repeatability conditions, and the concentration from the CRM are quadratically combined.

3.1.7.1. Combined Standard Uncertainty for All the Sources of Uncertainty

$$u_{com} = \sqrt{(0.060)^2 + (0.0630)^2 + (0.0630)^2 + (0.000145)^2 + (0.0117)^2 + (0.1732)^2} = 0.2041$$

3.1.7.2. Combined Relative Uncertainty for All the Sources of Uncertainty

$$u_{r\ comb} = \sqrt{\left(\frac{0.060}{3}\right)^2 + \left(\frac{0.0140}{1}\right)^2 + \left(\frac{0.0154}{50}\right)^2 + \left(\frac{0.0630}{50}\right)^2 + \left(\frac{0.000145}{.30}\right)^2 + \left(\frac{0.0119}{3}\right)^2 + \left(\frac{0.1732}{100}\right)^2} = 0.0248$$

Table 10. Estimation of standard uncertainty and relative uncertainty for the certified reference materials used.

ID CRM	SRM ID	Element	Concentration mg/L	*U* CRM	*u* CRM	Rel. Std Unc.	Rel. Std. Unc.
ICP-MS-68B-A250	3103a	As	100	1.0	0.500	0.2887	0.002886
-	3105a	Be	100	0.6	0.300	0.1732	0.001732
-	3106	Bi	100	1.0	0.500	0.2887	0.002886
-	3109a	Ca	100	1.0	0.500	0.2887	0.002886
-	3108	Cd	100	0.6	0.300	0.1732	0.001732
-	3113	Co	100	0.6	0.300	0.1732	0.001732
-	3114	Cu	100	0.6	0.300	0.1732	0.001732
-	3126a	Fe	100	0.6	0.300	0.1732	0.001732
-	3141a	K	100	1.0	0.500	0.2887	0.002886
-	3127a	La	100	0.6	0.300	0.1732	0.001732
-	3129a	Li	100	1.5	0.750	0.4330	0.004330
-	3131a	Mg	100	0.6	0.300	0.1732	0.001732
-	3132	Mn	100	1.5	0.750	0.4330	0.004330
-	3152a	Na	100	1.0	0.500	0.2887	0.002886
-	3136	Ni	100	1.0	0.500	0.2887	0.002886
-	3139a	P	100	0.6	0.300	0.1732	0.001732
-	3128	Pb	100	0.6	0.300	0.1732	0.001732
-	3148a	Sc	100	1.0	0.500	0.2887	0.002886
-	3153a	Sr	100	0.6	0.300	0.1732	0.001732
-	3164	U	100	0.6	0.300	0.1732	0.001732
-	3165	V	100	1.0	0.500	0.2887	0.002886
-	3168a	Zn	100	0.6	0.300	0.1732	0.001732
ICP MS-68B-B-500	3151	Ag	100	1.0	0.500	0.2887	0.002886
-	3134	Mo	100	1.0	0.500	0.2887	0.002886
-	3102a	Sb	100	1.0	0.500	0.2887	0.002886
-	3161a	Sn	100	1.0	0.500	0.2887	0.002886
-	3163	W	100	2.0	1.000	0.5774	0.005773
HPS Sulfur 100054-5-250	3154	S	1000	5.0	2.500	1.4434	0.001443

3.1.8. Percentage of Combined Relative Uncertainty for All Sources of Uncertainty

$$\%\, u_{r\ comb} = 2.48$$

3.1.9. Expanded Uncertainty Considering All Evaluated Sources of Uncertainty

$$U_{exp} = u_{com} * 2 = 0.2041 * 2 = 0.4082$$

Similarly, the combined standard uncertainty (CSU), combined relative uncertainty (CRU), percentage relative uncertainty (%CRU) and expanded uncertainty (*U*exp) were obtained for the remaining 28 chemical elements evaluated. These values are presented in Table 11.

Table 11. Estimation of combined standard uncertainty, combined relative uncertainty, percentage relative uncertainty, and expanded uncertainty considering all evaluated sources of uncertainty.

Element	Combined standard uncertainty (CSU)	Combined relative uncertainty (CRU)	Percentage relative uncertainty (% CRU)	Expanded uncertainty (*U*)
Ag	0.0425	0.0125	1.25	0.0850
As	0.0948	0.0467	4.67	0.1896
Ba	0.0814	0.0346	3.46	0.1628
Be	0.1385	0.0415	4.15	0.2770
Bi	0.1313	0.0337	3.37	0.2626
Ca	0.0854	0.0510	5.10	0.1711
Cd	0.0936	0.0348	3.48	0.1872
Cu	0.1439	0.0307	3.07	0.2878
Co	0.0600	0.0364	3.64	0.1200
Fe	0.0919	0.0577	5.77	0.1838
K	0.0930	0.0332	3.32	0.1860
La	0.0626	0.0578	5.78	0.1252
Li	0.1603	0.0366	3.66	0.3206
Mg	0.0804	0.0329	3.29	0.1608
Mn	0.0900	0.0369	3.69	0.1800
Na	0.0591	0.0343	3.43	0.1182
Ni	0.0836	0.0320	3.20	0.1672
P	0.0808	0.0354	3.54	0.1616
Pb	0.1354	0.0414	4.14	0.2708
Sc	0.5156	0.0816	8.16	1.0312
Sr	0.2474	0.0368	3.68	0.4948
U	0.0910	0.0319	3.19	0.1820
Va	0.0848	0.0311	3.11	0.1696
Mo	0.0593	0.0297	2.97	0.1186
Sb	0.0844	0.0362	3.62	0.1688
Sn	0.2062	0.0366	3.66	0.4124
S	0.0706	0.0393	3.93	0.1412
W	0.0944	0.0317	3.17	0.1888
Zn	0.0948	0.0505	5.05	0.1896

3.1.10. Sources of Uncertainty that Contribute to the Estimation of Relative Uncertainty

Figure 3 shows the contribution of the sources of relative uncertainty that contribute the most uncertainty to the measurement method. As can be seen, these are the concentration from the calibration curves and the volumetric material in the case of the determination of aluminum. Similar results are observed for the rest of the 28 chemical elements evaluated.

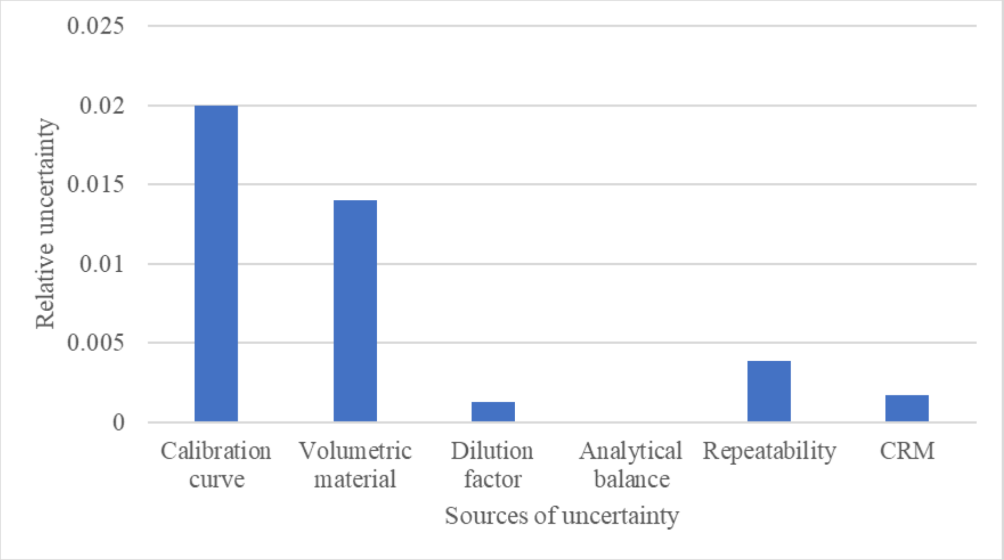

Figure 3. Graphical contribution of the sources of relative uncertainties considered in this research.

4. Discussion

4.1 Measurement Method Validation

The results confirm that the analytical method was successfully validated for the simultaneous quantification of 29 chemical elements using the ICP-OES technique. This method demonstrates high efficiency for multielemental analysis, offering substantial reductions in both analysis time and overall cost [8,9]. Although the initial investment in instrumentation and consumables for ICP-OES can be relatively high, the advantages—such as analytical versatility, high sensitivity, strong tolerance to total dissolved solids, and the capability for simultaneous detection—make it a cost-effective option in the long term [22,24]. Regarding method validation, the R^2/R values ranged from 0.9972/0.9982 for Be to 1.0000/1.0000 for elements such as Ag, Bi, and Co. These values exceed the commonly accepted minimum threshold of $R^2/R \geq 0.9950$ for chemical measurements [25]. Similar validation outcomes have been reported by Frazzoli and Bocca (2008) [28], who analyzed As, Pb, and Cd in cow serum and infant milk formulas using ICP-MS, as well as by Rodríguez-Giraldo et al. (2022) [29], who determined Cd in cacao almonds. Overall, the linearity results obtained through calibration curve analysis align with those reported by other researchers applying the ICP-OES technique across diverse sample types [30–32].

Regarding the results obtained for LOD/LOQ, values ranged from 0.001/0.01 µg/L for Co to 0.081/0.81 µg/L for nickel Ni. These values are consistent with those reported by Rodríguez-Giraldo et al. (2008) [29] for Cd in cacao almonds. In contrast, Sereshti et al. (2012) [30] reported higher LOD/LOQ values ranging from 0.13/0.43 µg/L for Al to 0.52/1.72 µg/L for Ti in water samples, using an ultrasound-assisted emulsification microextraction system optimized for the simultaneous determination of 12 elements by ICP-OES. The results obtained in the present study are broadly comparable with those reported in the literature for a variety of sample matrices analyzed using the ICP-OES technique [33–36].

Regarding the assessment of accuracy under repeatability conditions, as evaluated through CV, the results ranged from 0.72% for Mg to 6.82% for Ag. However, it is important to note that a CV of 20.04 was observed for Sn, which significantly exceeds the generally accepted threshold. This result is considered an outlier, as the majority of elements analyzed fell within the acceptable range. The elevated variability for Sn may be attributed to issues related to extraction efficiency or calibration inconsistencies. Similar challenges have been documented by Heltai et al. (2015) [37], who reported calibration difficulties with ICP-OES during multielement analysis in a sequential extraction procedure for heavy metal fractionation in aquatic sediments, particularly affecting Cd and Zn. Comparable findings have also been reported by other researchers across various sample matrices analyzed using ICP-OES [38–41].

4.1.2. Estimation of Measurement Method Uncertainty

The primary sources of uncertainty evaluated in this study included the concentration derived from calibration curves, volumetric equipment, dilution factor, analytical balance, accuracy under repeatability conditions, and CRMs. Aluminum was used as a representative example for the estimation of combined standard uncertainty, relative uncertainty, and expanded uncertainty, although the same procedure was applied to the other 28 chemical elements analyzed by ICP-OES. For Al, the combined standard uncertainty was 0.2041 µg/L, corresponding to a combined relative uncertainty of 0.0248 (2.48%). The expanded uncertainty, calculated using a coverage factor (κ) of 2 for a 95% confidence level, was 0.4082 µg/L. These results are considered highly satisfactory, indicating robust internal quality control within the laboratory. This performance can be attributed to regular calibration of materials and instrumentation, ensuring reliable metrological traceability. Comparable results were obtained for the remaining elements. Notably, the overall combined uncertainty percentage of 3.42% was lower than values reported by other studies employing ICP-OES or ICP-MS for a range of biological and inorganic matrices [42–45].

In addition, the most significant contributors to the overall uncertainty were the concentration derived from the calibration curve (0.020 µg/L) and the volumetric equipment (0.0140 µg/L). Marques et al. (2016) [46] reported that the primary source of uncertainty in their study was the recovery percentage, whereas Tanase et al. (2015) [47] identified concentration from calibration curves and measurement repeatability as the most influential factors. Worsfold et al. (2019) [48] emphasized that accuracy is typically the dominant source of uncertainty, as it most realistically reflects the overall method validation process.

Furthermore, several researchers have highlighted the importance of incorporating CRMs in the estimation of analytical uncertainty [49–52]. They have also underscored the critical role of the pre-analytical phase, including calibration of materials and laboratory equipment, sample weighing, and the wet digestion process (using either a heating plate or a microwave system), as a potential source of uncertainty in analytical measurements [53–57].

Fathabad et al. (2018) [58] emphasize that uncertainty estimation is essential when determining the concentration of heavy metals in biological samples intended for human consumption, such as processed fruit juices, as the results are directly linked to potential health risks. In this context, they recommend the use of the Monte Carlo simulation method for uncertainty estimation. Similarly, Pirsaheb et al. (2021) [59] advocate for the Monte Carlo simulation approach in estimating uncertainty related to the determination of heavy metals in cereals, with the aim of evaluating health risks associated with the consumption of contaminated food products.

In contrast to these approaches, Mijatović et al. (2019) [60] propose estimating measurement uncertainty using the Nordtest concept, specifically through a recovery test approach. This method categorizes uncertainty into two main components—accuracy and trueness—while excluding other potential sources of uncertainty from the estimation process.

5. Conclusions

The analytical method based on ICP-OES was successfully validated, and its measurement uncertainty was estimated in accordance with ASTM E2941-14. The validation results demonstrated acceptable linearity, with R^2 values ranging from 0.9972 to 1.0000 and R values ranging from 0.9982 to 1.0000, thus meeting the acceptance criterion ($R^2/R \geq 0.995$). Accuracy under repeatability conditions yielded acceptable CV values between 1.0% and 8.0%. Trueness evaluation revealed no significant bias, with recovery rates within the acceptable range of 100% ± 10%. Trueness analysis revealed no significant bias, and recovery rates remained within the acceptable range of 100% ± 10%. Combined uncertainties ranged from 0.0425 to 0.5156 µg/L, while relative uncertainty percentages varied from 1.25% to 8.16%. The primary contributors to relative uncertainty were the concentration values derived from calibration curves and the use of volumetric equipment.

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