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Comparison Between Analytical Results of ICP Techniques for the Determination of Arsenic in Water Matrices

Ricardo Crubellati*, Liliana González, Hugo Achear, Daniela Cirello Servicio Geológico Minero Argentino, Instituto de Tecnología Minera, Argentina.

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Abstract: In this paper, a comparison between two different analytical methods is described for arsenic determination. Water samples were directly determined for arsenic using inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Data from the study demonstrate differences in the accuracy of the analytical results depending on the As level concentration. Uncertainty plays an important role in this study.

Keywords: Arsenic, Analytical Chemistry, ICP-OES, ICP-MS, Environmental analysis

1. Introduction

Arsenic is a toxic element that is regularly required as a determinant in a suite of elements for many laboratories.

Eight methods are currently approved in 40 CFR 141.23 for the analysis of arsenic in drinking water. Only two of these methods (Inductively Coupled Plasma-Atomic Emission Spectrometry (ICPAES) (Standard Methods 3120 B) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Standard Methods 3125) are multi-element or multi-analyte, meaning other analytes besides arsenic can be measured during the analysis.

The recommended guideline value of the World Health Organization for arsenic in drinking water is 0,01 mg/L (WHO, 2011). However, in many places, a new value of 0,005 mg/L has been adopted. For this reason, all chemical laboratories have to work in the future trying to adapt methods for reaching this new value.

In this paper, we made a comparison between two ICP methods regarding the detection limit of each technique and studying the different results in the range where both methods are acceptable.

2. Methods

For the experiments, a Perkin Elmer Optima 5300 DV Inductively Coupled Plasma Optical Emission Spectrometer, equipped with concentric nebulizer and cyclonic spray chamber for use with aqueous matrices (ICP-OES) and a Perkin Elmer ICP Mass Spectrometer Elan DRCe were used.

For ICP-OES, the 188.98 nm wavelength for As was used, and the best conditions to lower the detection limit were studied.

Corresponding author:

Ricardo Crubellati, Servicio Geológico Minero Argentino, Instituto de Tecnología Minera, Argentina, Research field: Analytical Chemistry. E-mail: ricardo.crubellati@segemar.gov.ar.

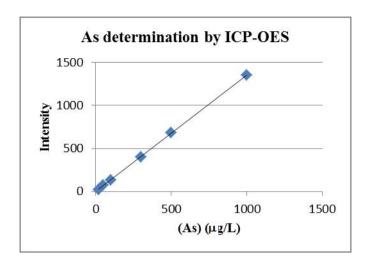


Fig 1. Calibration curve for As by ICP-OES.

LD (detection limit) and LQ (quantification limit) for As were 20 and 6.0 μ g/L, respectively. For ICP-MS, the determination was carried out at mass 75.

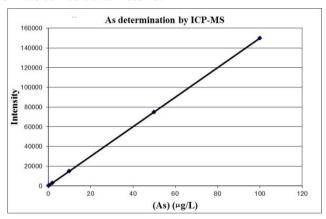


Fig 2. Calibration curve for As by ICP-MS.

LD (detection limit) and LQ (quantification limit) for As were 0.05 and 0.15 μ g/L, respectively. Both methods have a range (6 -100 μ g/L) where it is possible to use any of both methods interchangeably.

3. Results and Discussion

We made a study between both techniques through the participation of the laboratory in proficiency tests (PT) with Environmental Canada. The idea was the evaluation and comparison of analytical results produced by ICP-OES and ICP-MS, taking into account that in many samples, it was possible the determination indistinctly by one method or the other one.

Ten water samples were distributed between approximately 30 laboratories all over the world to determine about 30 analytes. In the case of As, concentration values were between 1 and 160 μ g/L.

The samples for arsenic were analyzed using both ICP methods.

142 Comparison Between Analytical Results of ICP Techniques for the Determination of Arsenic in Water Matrices

For those samples below the LQ for ICP-OES, only the results with ICP-MS are reported. In the other cases, both results were reported, taking into account future accreditation of both tests by OAA (Argentine Accreditation Body).

Table 1 shows the assigned value and both results (in µg As/L).

Table 1. Assigned value and ICP-OES and ICP-MS results.

Assigned value	ICP-OES result	ICP-MS result
9.9	< 6	1.1 ± 0.1
6,19	< 6	6.1 ± 0.2
8,69	8.9 ± 1.6	$8,4 \pm 0,3$
15,4	16.7 ± 2.0	$15,1 \pm 0,6$
19,8	$20,6 \pm 2,2$	$19,1 \pm 0,0$ $19,1 \pm 0,7$
25,4	$24,0 \pm 2,7$	$25,0 \pm 1,0$
27,0	29 ± 3	$26,0 \pm 1,0$
40,9	42.2 ± 3	40.0 ± 1.6
81	77 ± 4	73 ± 3
162	163 ± 7	155 ± 10

Percent deviation from assigned value

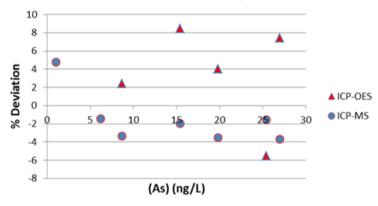


Fig 3. Percent deviations for low As concentrations.

Percent deviation from assigned value 10 8 6 4 2 0 5 10 15 20 26 30 ICP-OES 4 -6 -8 (As) (ng/L)

Fig 4. Percent deviations for high As concentrations.

Comparing the results (Figures 3 and 4), it can be seen that below concentration values of 40 μ g/L, ICP-MS results are more accurate. For values between 40 and 80 μ g/L, both results are similar in accuracy, and above concentration values of 80 μ g/L, it is better to report results from ICP-OES.

4. Conclusions

In analytical chemistry, it is not correct to consider only the analytical result of a measurement, but the uncertainty associated must be also considered.

In ICP-MS, as it is shown in Table I, uncertainty is lower than the equivalent one in ICP-OES for values below 40 μ g/L. For this reason, in that range, results are more reliable.

In contrast, for results above 80 µg/L, uncertainty in ICP-OES is lower than the equivalent one in ICP-MS. This is largely due to the dilution of samples made prior to the As determination analysis by ICP-MS.

In general, all study results in the laboratory were satisfactory (Z score). Nevertheless, it was possible to evaluate bias and uncertainty in PT to be able to establish a relation between these parameters.

From this evaluation, it was concluded that depending on the As concentration values, it is better to choose ICP-OES or ICP-MS. Only in the range $40 - 80 \mu g/L$, it is possible to use indistinctly any of both techniques.

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