



Comparison between Methods Using Thallium and Indium as Internal Standard for the Determination of Trace Elements in Water Samples by ICP-MS

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1. Introduction

Trace element analysis in environmental samples is usually part of an Environmental Monitoring Program and can be performed using different analytical techniques. The Inductively Coupled Plasma Mass Spectrometry (ICP-MS) technique is one of the most efficient for the determination of trace elements, but to ensure reliable results the equipment calibration is essential and the method that best fits the type of analysis performed must be evaluated. In this work, the calibrations that best fit the analytical study are: the external calibration, which consists of the construction of analytical curves from the reading of known and increasing concentrations of a U standard; and the other is the internal calibration, which has the purpose of correcting fluctuations in the equipment's signal, and consists of the addition of an internal standard with physicochemical characteristics similar to the U-238 analyte, with thallium and indium being the options selected for the analyte.

The main objective of this work is to compare two methods for the determination of U-238 in water using ICP-MS with external and internal calibration on both methods, however, one of them using thallium (Tl) as an internal standard on the internal calibration and the other indium (In). This study will allow the development of a quality control method for standards, as well as the choice of the analysis method according to available resources.

2. Methodology

A total of 127 water samples (surface, underground, atmospheric) were collected in a rural Brazilian area and were analyzed by ICP-MS. In the thallium method, the internal standard was added directly to the sample, while the indium one was introduced into the equipment simultaneously with the sample and externally to it. To ensure the reliability of the results and validate the calibration curves, reference samples from the National Intercomparison Program (PNI) were analyzed, obtaining an ideal deviation of less than 10% between the known value from the reference samples and the results obtained in the analysis. In addition, for quality control of standards and materials during the analysis, and even to increase the reliability of the results and certify the absence of contamination, blank samples were interspersed between measurements, obtaining results close to 0 $\mu\text{g.L}^{-1}$ in both methods.

3. Results and Discussion

The statistical comparison of obtained analytical results was performed using ProUCL 5.1 software, provided by the Environmental Protection Agency (EPA), and the nonparametric Wilcoxon-Mann-Whitney test. The comparison indicated that the results obtained in the two analytical procedures were statistically equivalent. Only 10,3% of the analyzed samples presented a difference in results greater than 20% between the two methods (Figure 1), which may be related to the correction of indium to the equipment fluctuations in the analysis of samples with lower concentrations, possibly due to the greater difference between its atomic mass and that of U-238. Or even, these small differences in the analysis of sample with low concentrations can be related to the introduction of the In as internal standard, that is made simultaneously and externally to the sample, so if there was a flux variation for a brief moment it could influence more samples with lower analyte concentrations than with higher ones.

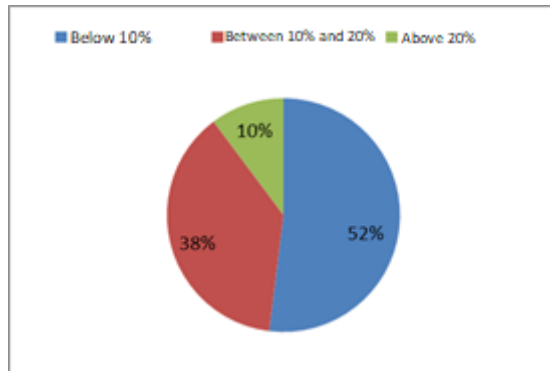


Figure 1: Representation of sample quantities in relation to the difference between the results obtained in each method

4. Conclusions

Thus, it can be concluded that both the thallium method and the indium one, studied in this work, can be used for the analysis of U-238 in water samples, both being reliable and statistically equivalent methods. This allows the analyst to choose the most suitable analytical method for the work, as well as enable the identification of suspicious results or evaluation of the quality control of the laboratory's internal standards.

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