



Optimization of Analysis Methodology in the Determination of Cd, In and Impurities in Nuclear Grade Silver-Indium-Cadmium Alloys

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1. Introduction

The control of the reaction and the homogenization of the power distribution in the core in order to compensate for the excess reactivity during the burning is carried out by control bars in most pressurized water type reactors (PWR). These bars are manufactured with neutron absorbing materials in the composition of Ag-15In-5Cd [1, 2].

Silver-Indium-Cadmium alloys have interesting nuclear properties, since silver and indium have a thermal cross section with large absorption for epithermic resonance. Cadmium, on the other hand, has a high cross section (2450 barns), increasing the capacity to absorb thermal neutrons. However, it is known that increasing the percentage of cadmium beyond 5% by weight does not improve the neutron absorption capacity, mechanical properties or corrosion resistance [3]. The ASTM C752 standard stipulates, in addition to the alloy constituents, the total values of impurities (0.05 % max.), lead (0.03% max.) and bismuth (0.03%) [4], foreseen for this specific grade of metal alloy.

As can be seen, the quantities of elements in the alloy have specific functions for the satisfactory performance of the absorber bars. To evaluate the chemical composition of these nuclear grade alloys, the most used characterization method is titrimetry. Thus, for the determination of the silver content, the ASTM C760 standard establishes the use of potentiometric titration and, for indium and cadmium, the complexometric titration is used [5]. The titration method is a procedure performed in several steps that, consequently, requires a large execution time [6].

However, this can be avoided with the use of the multi-element technique with inductively coupled plasma optical emission spectrophotometry – ICP OES. This technique has the advantage, when compared to the titrimetry method, of having greater precision, accuracy, sensitivity and speed [7].

In the multi-element determination, in the ICP OES, the solution is nebulized, and then the aerosol containing the sample goes through the existing desolvation, vaporization, dissociation, atomization, excitation and ionization processes [7].

This work aims to establish a methodology for determining the alloying elements for the Ag-In-Cd alloy and its impurities using the ICP OES method.

2. Methodology

2.1. Determination of alloy elements (Cd and In)

To determine the elements (Cd and In) of the Ag-15In-5Cd alloy, 0.01 g of samples were dissolved with 60 mL of nitric acid PA in a heated plate in the range of 150 to 170 °C in a glass beaker of the tall barrel type and, after total dissolution, the content was analytically transferred to a 100 mL volumetric flask and increased with ultrapure water to a volume of 100 mL, thus maintaining the acidic medium at a concentration of 8M necessary to maintain stability of the elements present.

Spectral lines (λ) free from interferences were selected for In and Cd. The selected lines as well as the position of the background signal, the sensitivity (Sens.) and the detection limit (LD) were experimentally

determined.

The selectivity was determined by measuring the analytical signal of the major elements present in the alloy (Ag, Cd, In), experimentally determining the sensitivity of each element in the respective lines and calculating the interference coefficient (S_i/S_a) according to the Equation 1.

$$\frac{S_i}{S_a} = \frac{I\lambda_i/C_i}{I\lambda_a/C_a} \quad (1)$$

Where: S_i : interferent sensitivity, $I\lambda_i$: interferent intensity at wavelength, C_i : interferent concentration, S_a : analyte sensitivity, $I\lambda_a$: analyte intensity at wavelength, C_a : analyte concentration.

In order to assess the method's ability to measure the accuracy of the elements, three solutions of alloying elements (Ag, In and Cd) were analytically prepared from pure metals at a concentration of about 1000 ppm each and mixed in the proportion of the alloy (80- 15-5%).

To assess the robustness of the method due to possible variations, the factors shown in Table I were considered and the tests carried out on different dates.

Table I: Factors considered for the assessment of Robustness

Factor	Nominal	Variation
Sample mass	0.01 (g)	0.011 (g)
Acid Molarity	8.0 M	8.5 M
Plate Temperature	150 °C	170 °C
Heating Time	10 minutes	12 minutes
Agitation	No	Yes

2.2 Determination of impurities

For the determination of impurities, 0.1 g of samples were dissolved with 60 mL of nitric acid PA in a heated plate in the range of 150 to 170 °C in a tall glass beaker and, after total dissolution, the content it was analytically transferred to a 100 mL volumetric flask and increased with ultrapure water to a volume of 100 mL, thus maintaining the medium with an acidity of 8M necessary to maintain the stability of the elements present.

Spectral lines (λ) free from interferences for impurities were selected. The selected lines, as well as the position of the background signal, the sensitivity (Sens.) and the detection limit (LD) were determined experimentally.

The selectivity was determined by measuring the analytical signal of the impurity elements considered for the Ag-Cd-In alloy, experimentally determining the sensitivity of each element in the respective lines and calculating the interference coefficient (S_i/S_a) according to the Equation 1.

To assess the effectiveness of the method in determining impurities, four aliquots were prepared with the sample of the fusion studied and, in three of them, the equivalent of 0.03% of the elements lead and bismuth were added already in the opening process and performed three measures of each mass. The recovery was calculated and the values of the recovery indexes (RI) can be seen in Table IV.

3. Results and Discussion

3.1. Determination of alloy elements (Cd and In)

From Equation 1, it was observed that the greatest interference found was cadmium in the spectral line of indium with a magnitude of only 0.12%.

For both elements, a recovery rate was close to 100% and a low level of internal variation for their individual measurements can be observed in Table II.

Table II: Recovery index for Cd and In elements

Measurements	Results (ppm)	
	Cd	In
Mean	51.04	146.83
Standard deviation	0.66	1.37
RSD	1.3	0.9
Prepared concentration (ppm)	50.41	150.40
Recovery index (%)	101.25	97.63

The robust mean and robust standard deviation found can be considered a closer to true measure of the precision and accuracy of the method. The *C/c* factor that is calculated as a function of variations and nominal values are very close to zero, thus the method is robust to these studied variations, as shown in Table III.

Table III: Results obtained in the Robustness Test

Results	Cd	In
Robust mean	5.03	15.08
Robust standard deviation	0.02	0.02
RSD	0.4	0.1
<i>C/c</i> Factor	0.01	0.01

3.2. Determination of impurities

From Equation 1, it was observed that the greatest interference found was that of zirconium in the spectral line of silicon and of a magnitude less than 5%.

For both elements, a recovery rate greater than 90% and an internal variation level for their individual measurements of 6.2 and 4.0% for the elements lead and bismuth, respectively, can be observed in Table IV.

Table IV: Values obtained from recovery rates (RI)

Measurements	Results (%)	
	Pb	Bi
Mean	0.027	0.028
Standard deviation	0.002	0.001
RSD	6.2	4.0
Quantity added (%):	0.030	0.030
RI (%):	90.70	92.24

4. Conclusions

From the results obtained in this work, it could be observed that the ICP OES technique reached the proposed objectives for the determination of cadmium, indium and impurities contents. When observing the values of the spectral selectivity of indium and cadmium, there was a coefficient with a value close to zero and that the greatest interference found was cadmium in the spectral line of indium with a magnitude of only 0.12%.

Regarding the recovery test of alloying elements (In and Cd), a recovery rate close to 100% and a low level of internal variation for its individual measurements were observed. Still, it could be observed that the influence of the technical variables by the robustness analysis obtained a robust mean and a robust standard deviation. Thus, they can be considered a measure closer to the real one of the precision and accuracy of the method. The *C/c* factor, which is calculated as a function of variations and nominal values, is very close to

zero, thus the method is robust to these studied variations.

Regarding the determination of impurities, the selectivity coefficients in the Ag-In-Cd alloy obtained are all close to zero, and the greatest interference found was that of zirconium in the spectral line of silicon and of a magnitude lower than 5%.

Taking the Pb and Bi contents, for both elements it is possible to observe a recovery rate greater than 90% and an internal variation level for their individual measurements of 6.2 and 4.0% for the elements lead and bismuth, respectively.

Thus, it was demonstrated that the use of the ICP OES technique is capable of being safely used in the chemical characterization of nuclear grade alloy elements.

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