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Validation Analysis Methodology to Determine the Cadmium, Indium and Impurities Concentration in Nuclear Grade Silver-indium-cadmium Alloys

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ABSTRACT

This work aims optimized to set up and an analytical method for a reliable determination of silver-indium-cadmium alloy constituents and their impurities through the use of ICP OES (Inductively coupled plasma optical emission spectrometer). It has greater precision, accuracy, and sensitivity when compared to the traditional methodology. The validation process was carried out according to INMETRO's (Instituto Nacional de Metrologia, Qualidade e Tecnologia) Analytical Method Validation Guidance.

Keywords: **control rod, absorber material, nuclear reactor, ICP OES, analytical validation**

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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 stablishes, 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 alloy. It also stablishes the total values of impurities (0.05 % max.), lead (0.03% max.) and bismuth (0.03%) [4].

The quantities of elements in the alloy have specific functions for the satisfactory performance of the absorber bars and to evaluate the chemical composition of these nuclear grade alloys, the most used characterization method is titrimetry. The ASTM C760 standard establishes the use of potentiometric titration for the determination of the silver content and for the determination of indium and cadmium content, 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. When compared to the titrimetry method, this technique has the advantages of greater precision, accuracy, sensitivity and speed [7].

In the multi-element determination by using 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].

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In excited atoms, electrons emit radiation when returning to their ground state, with a wavelength that allows identifying the emitting element, according to Equation 1 [8]:

$$\Delta\mathrm{E}=\mathrm{E}_1-E_0=\mathrm{h}\nu=\mathrm{hc}/\lambda \tag{2}$$

Where: $\Delta\mathrm{E}$ is the change in energy between the atom in the ground state (E_0) and the excited one (E_1)h, is Plank's constant, ν is the frequency of radiation and λ is the wavelength [8].

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. The analytical validation process was carried out according to INMETRO's (Instituto Nacional de Metrologia, Qualidade e Tecnologia) Analytical Method Validation Guidance [9]

2. MATERIALS AND METHODS

2.1 Determination of alloy elements (Cd and In)

To determine the alloying elements (Cd and In), 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 tall form glass beaker and after the total dissolution to content was analytically transferred to a 100 mL volumetric flask and filled with ultra-pure water until 100 mL volume, thus maintaining the solution with an acidity of 8M necessary to maintain the stability of the elements present.

The ICP OES instrument and operational description used in this experiment is presented in table 1.

Spectral lines (λ) free from interferents 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 (DL) were experimentally determined and are shown in the table 2.

Table 1: Operation parameters for ICP OES

ICP OES Equipment brand	Spectroflame Modula - SPECTRO
Frequency	27.12 MHz

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Operating power	1.2 kW
Plasma gas flow	25 L/min
Aerosol flow	0.8 L/min
Nebulizer type	Cross flow
Spray Chamber type	Scott

Table 2: Spectral lines used in the determination of alloying elements (In and Cd) in the composition of the Ag-In-Cd alloy. The sign background refers to the distance from the count position of the sign with the (-) sign for left and (+) sign for the right.

Line	λ (nm)	Position of background sign	Sens. (cps/ppm)	DL (ppm)
Cd	226.502	(-)0.022, (+)0.058	5238	0.0099
In	303.936	(-)0.026	231	0.2808

2.2 Impurities determination

For the determination of impurities, 0.1 g of samples was 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 was transferred analytically to a 100 mL volumetric flask and filled with 100 mL of ultra-pure water, thus keeping the solution with an acidity of 8M necessary to maintain the stability of the elements present.

The ICP OES instrument and operational description used in this experiment is presented in table 3.

Spectral lines (λ) free from interferents for impurities were selected. The selected lines as well as the position of the background signal, the sensitivity (Sens.) and the detection limit (DL) were experimentally determined and are shown in Table 4.

Table 3: Experimental system and operating parameters

Equipment brand	JY HORIBA ULTIMA 2
Frequency	40 MHz
Operating power	1.0 kW
Plasma gas flow	16 l/min
Aerosol flow	0.6 l/min
Nebulizer type	Meinhard
Spray Chamber type	Ciclonyc

Table 4: Spectral lines used in the determination of Ag-In-Cd alloy impurities. The sign background refers to the distance from the count position of the sign with the (-) sign for left and (+) sign for the right. The DL of the method considers the minimum value that can be obtained from the LD of the spectral line, the mass of the used aliquot and the final volume of the dilution.

Line	λ (nm)	Signal background Position (nm)	Sens. (cps/ppm)	DL (ppm)	DL method (%)
Al	167.020	-0.02779	98349	0.0066	0.00066
Pb	168.155	-0.02082	11443	0.0497	0.00497
P	178.234	-0.01718	14529	0.0228	0.00228
Mo	203.844	-0.01856	16312	0.0163	0.00163
Bi	223.061	-0.02571	14409	0.0075	0.00075
Ni	231.604	+0.0236	14485	0.0025	0.00025
Fe	238.204	-0.02585	161674	0.0067	0.00067
Si	251.611	-0.01905	12819	0.0452	0.00452
Mn	257.610	+0.02571	14661171	0.0003	0.00003
Mg	279.553	-0.02452	1660307	0.0011	0.00011
Cr	284.325	-0.01820	161735	0.0204	0.00204
Cu	327.396	-0.02368	140378	0.0022	0.00022
Ca	393.366	-0.02377	1379890	0.0030	0.00030
Na	588.995	+0.03308	17197	0.0170	0.00170
Sn	189.918	-0.02377	16307	0.0117	0.00117
As	193.695	+0.02787	15150	0.0581	0.00581
Zn	213.856	+0.02383	14979	0.0022	0.00022
B	249.773	+0.02537	152752	0.0139	0.00139
V	309.311	+0.01284	136612	0.0008	0.00008
Be	313.107	+0.01906	1386499	0.0003	0.00003
Zr	327.305	-0.02704	147216	0.0017	0.00017
Co	345.351	-0.01235	14602	0.0241	0.00241

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 (Si/Sa) [10] according to the Equation 2.

$$\frac{S_i}{S_a} = \frac{\lambda_i / C_i}{\lambda_a / C_a} \qquad (2)$$

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Where: S_i is the interferent sensitivity, λ_i is the interferent intensity at wavelength, C_i is the interferent concentration, S_a is the analyte sensitivity, λ_a is the analyte intensity at wavelength and C_a is the analyte concentration.

3. RESULTS AND DISCUSSION

3.1 Selectivity of alloy elements (Cd and In) and impurities

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 (Si/Sa) [10] according to the Equation 2.

$$\frac{S_i}{S_a} = \frac{\lambda_i / C_i}{\lambda_a / C_a} \tag{2}$$

Where S_i is the interferent sensitivity, λ_i is the interferent intensity at wavelength, C_i is the interferent concentration, S_a is the analyte sensitivity, λ_a is the analyte intensity at wavelength and C_a is the analyte concentration.

In this way it is possible to measure the interference of each element in the chosen spectral line, the closer to zero, the smaller is the interference. The determined values are shown in Table 5 for alloy elements and Table 6 for impurities.

Table 5: Interference coefficients

	Interfering		
Line	**Cd**	**In**	**Ag**
Cd	1.0000	0.0000	0.0001
In	0.0012	1.0000	-0.0001

The coefficients are all close to zero, and the greatest interference found was that of cadmium in the spectral line of indium and of a magnitude of only 0.12%.

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Table 6: Interference coefficients for the considered impurity elements

Lines	Interfering												
	Al	**Pb**	**P**	**Mo**	**Bi**	**Ni**	**Fe**	**Si**	**Mn**	**Mg**	**Cr**	**Cu**	**Ca**
Al	1.0000	0.0002	0.0005	0.0004	0.0003	0.0005	0.0034	0.0036	0.0004	0.0005	0.0004	0.0007	0.0012
Pb	-0.0003	1.0000	0.0006	0.0001	0.0003	0.0002	0.0003	0.0006	-0.0002	0.0002	0.0002	0.0003	0.0003
P	0.0006	0.0007	1.0000	0.0005	0.0004	0.0004	0.0010	0.0006	0.0006	0.0006	0.0005	0.0005	0.0035
Mo	0.0000	0.0001	0.0002	1.0000	0.0001	0.0002	0.0001	0.0001	0.0001	0.0001	0.0000	0.0000	0.0001
Bi	0.0002	0.0002	0.0002	0.0002	1.0000	0.0003	0.0002	0.0002	0.0002	0.0002	0.0015	-0.0009	0.0002
Ni	-0.0004	-0.0005	-0.0004	-0.0004	-0.0004	1.0000	-0.0004	-0.0001	-0.0005	-0.0004	-0.0005	-0.0005	-0.0004
Fe	0.0002	0.0001	0.0001	0.0002	0.0001	0.0001	1.0000	0.0003	0.0002	0.0002	0.0015	0.0001	0.0026
Si	0.0026	0.0023	0.0024	0.0101	0.0027	0.0022	0.0022	1.0000	0.0024	0.0022	0.0025	0.0023	0.0037
Mn	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
Mg	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002	0.0001	0.0004	0.0003	1.0000	0.0001	0.0001	0.0070
Cr	0.0003	0.0003	0.0003	0.0002	0.0003	0.0003	0.0003	0.0003	0.0003	0.0002	1.0000	0.0003	0.0002
Cu	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
Ca	0.0008	0.0007	0.0006	0.0007	0.0008	0.0007	0.0008	0.0104	0.0006	0.0010	0.0009	0.0008	1.0000
Na	0.0026	0.0030	0.0027	0.0028	0.0024	0.0021	0.0027	0.0255	0.0031	0.0029	0.0021	0.0020	0.0032
Sn	0.0001	0.0002	0.0001	0.0001	0.0002	0.0001	0.0002	0.0001	0.0001	0.0001	0.0000	0.0002	0.0002
As	0.0012	0.0002	-0.0001	0.0003	0.0001	-0.0002	0.0005	0.0001	0.0001	0.0001	0.0000	0.0003	0.0003
Zn	0.0002	0.0001	0.0001	0.0001	0.0001	0.0053	0.0003	0.0004	0.0001	0.0001	0.0001	0.0039	0.0002
B	0.0001	0.0002	0.0003	0.0001	0.0003	0.0001	0.0003	0.0017	0.0001	0.0001	0.0002	0.0001	0.0001
V	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0010	0.0000	0.0000	0.0000
Be	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Zr	0.0003	0.0000	0.0002	0.0003	0.0001	0.0000	0.0002	0.0026	0.0016	0.0002	-0.0001	0.0005	0.0001
Co	-0.0003	-0.0005	-0.0006	0.0003	-0.0003	-0.0004	-0.0002	-0.0003	-0.0004	-0.0003	-0.0005	-0.0005	-0.0005
Ti	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0003	0.0000	0.0000	0.0001	0.0000	0.0000

The coefficients are all close to zero, and the greatest interference found was that of zirconium in the spectral line of silicon and of a magnitude less than 5%.

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3.2 Accuracy of alloy elements (Cd and In) and impurities

For the evaluation of the method's capability in the accuracy of the elements, three solutions of the alloying elements (Ag, In and Cd) were analytically prepared from the pure metals in a concentration of about 1000 ppm each and mixed in the proportion of the alloy (80-15 -5%). The results are shown in Table 7.

Table 7: Recovery index for Cd and In elements

Measurements	Results (ppm)	
	Cd	**In**
1	50.49	146.53
2	51.30	145.63
3	50.49	145.02
4	50.99	146.33
5	51.73	145.78
6	50.41	148.39
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**

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

To assess the effectiveness of the method for the determination of impurities, three aliquots were prepared with the sample of the alloy 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 three measurements were made. The recovery was calculated and the values of the recovery indexes (RI) can be seen in Table 08.

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Table 08: Values obtained from the Recovery Index (RI)

Measurements	**Results (%)**	
	Pb	**Bi**
Measure 1	0.029	0.027
Measure 2	0.029	0.029
Measure 3	0.030	0.029
Measure 4	0.025	0.027
Measure 5	0.025	0.028
Measure 6	0.027	0.027
Measure 7	0.025	0.027
Measure 8	0.026	0.028
Measure 9	0.027	0.027
Average	**0,027**	**0,028**
Standard deviation	**0,002**	**0,001**
RSD	6,2	4,0
Amount added (%):	0,030	0,030
IR (%):	**90,70**	**92,24**

For both elements, a recovery rate with a variation of less than 10% can be observed, an internal variation level for their individual measurements of 6.2 and 4.0%, for the elements lead and bismuth, respectively.

3.2 Robustness of alloy elements (Cd and In)

To assess the robustness of the method due to possible variations, the factors shown in Table 9 were considered and combined using the Youden and Steiner test [11], resulting in a combination of eight assays carried out on different days, where the mean and standard deviation are more realistic estimates of precision and accuracy.

The combinations of factors for alloy elements are shown in Table 10 and the results are shown in Table 11.

Table 9: Factors considered for the assessment of Robustness

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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
Warm up time	10 minutes	12 minutes
Agitation	No	Yes

Table 10: Combinations tested for the Robustness Test

Factor	**Combination**						
Sample mass	0.01	0.01	0.01	0.01	0.011	0.011	0.011
Acid Molarity	8.0	8.0	8.5	8.5	8.0	8.0	8.5
Plate temperature	150	170	150	170	150	170	150
Warm up time	10	10	12	12	12	12	10
Agitation	no	yes	no	yes	yes	no	yes
Results	**s**	**t**	**u**	**v**	**w**	**x**	**y**

Table 11: Results obtained in the Robustness Test.

Results (ppm)	**Cd**	**In**
s	5.01	15.10
t	5.03	15.09
u	5.05	15.10
v	5.04	15.06
w	5.04	15.06
x	5.07	15.05
y	5.01	15.09
z	5.02	15.09
Mean	**5.03**	**15.08**
standard deviation	**0.02**	**0.02**
RSD	0.4	0.1
C/c factor	0.01	0.01

The robust average and robust standard deviation found can be considered a more realistic measure of the method's precision and accuracy. The C/c factor that is calculated as a function of the variations and the nominal values are very close to zero, so the method exhibits robustness to the variations studied.

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4. CONCLUSION

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 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 method 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 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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REFERENCES

[1] W. K. ANDERSON, J. S. THEILACKER, Neutron Absorber Materials for Reactor Control, **Naval Reactors, Division of Reactor Development**, **US Atomic Energy Commission**, v. 7, p. 01-39, 1962.

[2] M. STEINBRÜCK, U. STEGMAIER, M. GROSSE, Experiments on silver-indium-cadmium control rod failure during severe nuclear accidents, **Annals of Nuclear Energy**, v 101, p. 347–358, 2017.

[3] M. CASTANHEIRA, L. TERREMOTO, J. SILVA, C. ZEITUNI, Análise da degradação de barras absorvedoras de nêutrons de Ag-In-Cd. Parte 1: Depleção da liga, efetividade de absorção de nêutrons e propriedades mecânicas, In: **INTERNATIONAL NUCLEAR ATLANTIC CONFERENCE**, 2002, Rio de Janeiro. 2002. p. 11-16.

[4] American Society For Testingand Materials – ASTM C752 –13. **Specification for Nuclear-Grade Silver-Indium-Cádmium Alloy**, 2016.

[5] American Society For Testingand Materials – ASTM C760 –90. **Standard Test Methods for Chemical and Spectrochemical Analysis of Nuclear-Grade Silver-Indium-Cadmium Alloys**, 2015.

ISSN: 2319-0612
DOI: https://doi.org/10.15392/2319-0612.2022.18
Submitted: 2022-12-16
Accepted: 2022-11-26

[6] Y. MOHASSAB, M. ELZOHIERY, F. CHEN, S. H. YONG, Determination of total iron content in iron ore and DRI: titrimetric method versus ICP-OES analysis, In: **EPD CONGRESS, 2016**. Springer, Cham, 2016. p. 125-133.

[7] A. C. DE C. BERNARDI, R. SOARES, V. ESCALEIRA, Comparação de técnicas analíticas para a determinação de cálcio, magnésio e alumínio trocáveis em amostras de solos, **Embrapa Solos-Circular Técnica (INFOTECA-E)**, 2003.

[8] C. F. PETRY, Determinação de elementos traço em amostras ambientais por ICP OES, **Dissertation**, Universidade Federal do Rio Grande do Sul, Porto Alegre, p. 73, 2005.

[9] DOQ-CGCRE-008 - REVISÃO 08. Orientação sobre Validação de Métodos Analíticos. INMETRO, Rio de Janeiro, JUN/2020.

10] M. I. Rucandio, "Estudio sobre la aplicación de la espectroscopía de emisión con fuente de plasma acoplado por inducción a la determinación de tierras raras", Ph.D Thesis, Universidad Autónoma de Madrid, 280 pp., CIEMAT, Madrid, Spain (1993).

[11] W. J. Youden, E. H. Steiner, Statistical manual of the association of official analytical chemists. AOAC International, Washington, D.C., USA (1975).

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