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DETERMINATION OF CHEMICAL ELEMENTS IN MAGNESIUM-BASED MATERIALS BY NEUTRON ACTIVATION ANALYSIS

Caio Almeida Justino da Silva[1], Isolda Costa[2], Jesualdo Luiz Rossi[2] and Mitiko Saiki[1]

[1] Centro do Reator de Pesquisas - CRPq
[2] Centro de Ciência e Tecnologia de Materiais - CCTM
Instituto de Pesquisas Energéticas e Nucleares (IPEN – CNEN/SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
caio.silva@ipen.br; icosta@ipen.br; jelrossi@ipen.br; mitiko@ipen.br

ABSTRACT

Over the last decades there was an increasing interest in using magnesium alloys for medical applications due to their biodegradability in the human body, providing a temporary mechanical support and corroding completely after the tissue healing. Although magnesium is a non-toxic element, it is of great importance to evaluate the element concentration, as well as the impurities present in both, pure magnesium and magnesium alloys, as the AZ31. The purpose of this study was to analyze the element composition of these materials using the method of neutron activation analysis (NAA). Standard Reference Materials (SRMs) acquired from National Institute of Standards and Technology (NIST) were analyzed for analytical quality control. Short and long term irradiations were carried out at the IEA-R1 nuclear research reactor and gamma-ray activities induced to the samples and element standard were measured using HPGe detector coupled to a Digital Spectrum Analyzer. The radioisotopes were identified by gamma ray energies and half-life. Concentrations of the elements As, Cr, Cd, Co, Fe, In, La, Mg, Mn, Mo, Na, Sb, V, W and Zn were determined in pure magnesium sample and the Al, As, La, Mg, Mn, Na, Sb and Zn in the AZ31 alloy, calculated by comparative method. The SRMs were analyzed by applying the same experimental conditions used for magnesium-based materials and their results presented good accuracy and precision. Thus, from the measurements obtained in this study it can be concluded that NAA is a suitable method for element determinations in magnesium-based materials providing reliable results.

1. INTRODUCTION

Nowadays, the industry of biomaterials that include medical devices of different types is considered as one of the markets of constant growth. A report that confirms this statement is that approximately 1 to 2.5 million of biomaterials units per year are manufactured in the world for applications such as in hip and knee prostheses, cardiovascular stents and in bone fixation plates [1].

Consequently, this fact has aroused great interest for the development of new types of biomaterials as well as for the improvement of existing ones. Magnesium alloys have been proposed in this scenario as biodegradable metals for temporary implants, leading to the absence of a new surgery to remove them, as is the case of cardiovascular stents and orthopedic prostheses [2]. These magnesium-based materials dissolve, that is, they fastly corrode in aqueous solutions, especially those containing chloride ions [3].

The use of magnesium-based materials is due to the fact that Mg is an essential element in the living organism. In addition, Mg is the cofactor element of more than 300 enzymatic

reactions in the body, such as DNA, RNA and protein synthesis [4]. Several studies have reported additional benefits of magnesium as antibacterial, osteoconductor and osteoinductor effects [5].

However, rapid degradation rates in physiological environments constitute the main limitation for these alloys essentially in degradation cases before cell healing [6-8]. The alloying elements and impurities can lead to formation of secondary phases, which present different potential from that of the matrix, facilitating or inhibiting the degradation rate [9]. Hence, an adequate chemical characterization of these materials is indispensable in a corrosion study. An instrumental technique that is reliable in elemental composition determination of metal alloys is the neutron activation analysis (NAA) [10-12], that was used in the present study.

According to Hamidatou [13], even with the appearance of new techniques of analysis, NAA still thrives in the analytical area mainly due to its unique advantage of high penetrating power of neutron and gamma rays. The NAA presents several advantages, such as high sensitivity for various elements, multielement analysis, in several types of matrices, small amount of sample required and no need of sample dissolution [14], which, in the case of alloys, present much difficulty.

The objective of this study was to analyze magnesium-based materials (pure magnesium, AZ31 alloy) by the NAA technique, in order to investigate their composition and the presence of impurities. These determinations are of interest in order to evaluate whether contents of elements are within the composition presented in the certificates, as well as to analyze the presence of impurities.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1 Magnesium-based materials samples

The magnesium-based materials analyzed in this study were: pure magnesium and magnesium alloy AZ31. The pure magnesium sample was obtained in ingot form and the magnesium alloy was acquired in sheet form with the dimensions of 30-x-30 cm^2 and 1 mm thickness. Preparation of these materials for analyses was carried out by cutting them in the form of chips with the aid of, bench top drill for the pure magnesium sample, and a steel pair of pliers for the Mg alloy. For elimination of possible contaminants, the samples were cleaned with acetone. Then, the acetone was removed and the samples were rinsed in a beaker with purified water (Millipore system), in which the chips stayed immersed for about two hours. The chips were separated from the liquid used and put on filter paper that was placed in a Petri dish. For drying, at room temperature, the Petri dish with the samples was kept inside a laminar flow cabinet.

In Figure 1, photographs of the chips are shown after preparation and cleaning, of (a) pure magnesium and (b) AZ31 alloy.

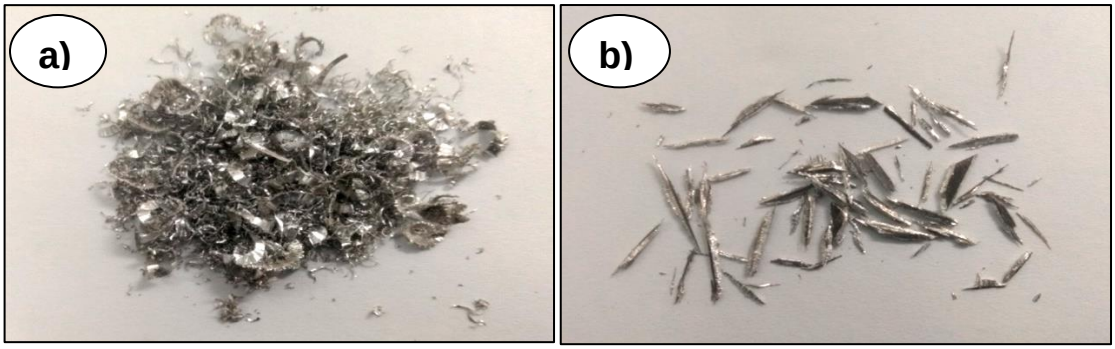

Figure 1: Photographs of pure magnesium (a) and AZ31 magnesium alloy (b) used from chemical analysis. Scale 1:1.

2.1.2 Certificated reference materials

In order to evaluate the quality of the results with respect to the precision and accuracy, three standard reference materials (SRMs) from the National Institute Standards Technology (NIST) were analyzed. These SRMs were: SRM 363 Chromium-Vanadium Steel Modified [15], SRM 1400 Bone Ash [16] and SRM 58a Ferrosilicon [17]. A biological SRM of 1400 Bone Ash was analyzed, since there is no metallic material certified for Mg element. The element concentration of this SRM 1400 was obtained in a dry weight basis, as recommended in the certificate. A moisture mass loss of 0.42 % was found to correct the Mg results. The moistures for metallic standard reference materials were considered negligible.

2.2 Experimental

2.2.1 Preparation of synthetic element standards

Certified standard solutions of elements purchased by Spex CertiPrep USA were used for preparing single and multielement solutions. In Table 1, are presented data of element standard solutions used in this study.

The synthetic element standards were prepared by pipetting aliquots (50-150 μL) of the standard solutions onto sheets of Whatman N° 40 filter paper. The calibration of the pipettor was previously verified before use. These filter sheets were dried at room temperature inside a desiccator and then placed into a clean polyethylene involucre which were sealed.

2.2.2 Neutron activation analysis procedure

Aliquots from 25 to 50 mg of samples and 25 to 100 mg for SRMs were weighed in polyethylene involucres using a Shimadzu analytical balance with a precision of 0.00001 g. The involucres were prepared using colorless polyethylene foils, previously cleaned with diluted solution of nitric acid P.A and purified water MilliQ. Two separate irradiations were used to determine elements having short and long-lived irradiations.

Table 1: Data of the standard solutions of elements used with their concentrations and mass of the irradiated elements.

Code of the Standard	Element	Element concentration (mg L^{-1})	Element mass used (μg)
Al2	Al	10004.00	1000.40
S6	As	30.00	1.50
	Cu	1999.92	100.00
	Mo	60.18	3.01
	Sb	12.03	0.60
L6	Cd	200.07	10.00
	Co	3.00	0.15
	La	12.00	0.60
Fe8	Fe	10009.00	500.25
In8	In	167.84	8.39
Mg3	Mg	10000.00	1500.00
Mn6	Mn	1000.0 0	50.00
N3	Na	4006.56	200.33
Ni1	Ni	10039.5	501.98
Ta9	Ta	100.20	5.01
V8	V	999.00	49.95
W1	W	200.60	10.03
Zn8	Zn	10011.00	500.55

Short-term irradiations from 10 to 30 s were carried out under a thermal neutron flux of 1.9 x 10^{12} n cm^{-2} s^{-1} for Al, In, Mg, Mn, Na and V determinations. The involucres containing sample and synthetic standards were placed in other polyethylene involucre that was inserted in a polyethylene device (called rabbit). The irradiation was performed using the "Pneumatic station IV" in the IEA-R1 nuclear reactor. For gamma activity measurements, the sample and the standards were mounted individually in a stainless steel planchet. A chronometer was used to record the times of the end of irradiation and the start and the end of counting for decay time correction. A counting system constituted of a Model GC 2018 Hyperpure Germanium detector coupled to a digital spectrum analyzer (DAS 1000) both from Canberra was used. The system had a resolution (FWHM) of 1.15 keV for 122 keV gamma-ray peak of ^{57}Co and 1.85 keV for 1332 keV gamma-ray peak of ^{60}Co. Each sample and standards were measured at least twice for different decay times and the counting times varied from 240 to 600 s. For acquisition the data of gamma-ray spectra and for processing the Genie 2000 Version 3.1 software from Canberra was used.

Eight-hour irradiations under a thermal neutron flux of about 4.5 x 10^{12} n cm^{-2} s^{-1} were performed for the determination of the elements As, Cd, Co, Cr, Cu, Fe, Mo, La, Ni, Sb, Ta, W and Zn. The samples and standards were wrapped in aluminum foil and then they were placed in a device (aluminum rabbit). After adequate decay times, standards and samples were also mounted in planchets and measured using the same counting system used for the case of short irradiation. Counting times ranged from 1800 to 50 000 s were used depending on the half-lives or activities of the radionuclides.

The radionuclides measured in both types of irradiation were identified according to their half-lives and gamma-ray energies. The radionuclides (half-life; gamma energy) used in this study were: ^{28}Al (2.24 min; 1778.99 keV), ^{76}As (26.32 h; 559.10 and 657.05 keV), ^{115}Cd (53.46 h; 527.91 keV), ^{60}Co (5.27 y; 1173.24 keV), ^{64}Cu (12.7 h; 1345.77 keV), ^{51}Cr (27.7 d; 320.08 keV), ^{59}Fe (44.5 d; 1099.25 keV), ^{116m}In (54.15 min; 1097.29 keV), ^{140}La (40.27 h; 487.02 and 1596,21 keV), ^{27}Mg (9.46 min; 843.76 and 1014.43 keV), ^{56}Mn (2.58 h; 1810.72 keV), ^{99}Mo (65.94 h; 140.51 and 739.58 keV), ^{24}Na (14.96 h; 1368.60 keV), ^{58}Co (70.82 d; 810.77 keV) for Ni determination, ^{122}Sb (2.70 d; 564.24 keV) ^{182}Ta (114.5 d; 1221.41 keV), ^{187}W (23.9 h; 479.57 keV), ^{52}V (3.75 min; 1434.08 keV) and ^{65}Zn (243.9 d; 1115.55 keV) [18].

The element concentrations were calculated by comparative method using the equation (1) [19].

$$C_s = \frac{m_{st} \cdot A_s \cdot e^{0.693(ts-tst)t_{1/2}}}{M_s \cdot A_{st}} \quad (1)$$

where C_s is the element concentration in the sample; m_{st} is the mass of the element in the standard; A_s and A_{st} are counting rates of the radioisotopes in the sample and in the standard, respectively; t_s and t_{st} are decay time for the sample and standard, respectively; M_s is the total mass of the sample and $t_{1/2}$ is the half-life of the radionuclide.

2.2.3 Treatment of the data

Statistical parameters of arithmetic mean, standard deviation, relative standard deviation and relative error were calculated for the results obtained in the analyses. Besides the Z-score values [20] were calculated using equation (2) in order to evaluate the accuracy of the results in the analyses of the standard reference materials.

$$\text{Z-score} = \frac{X_m - X_{ref}}{\sqrt{SD^2 + u^2_{(Xref)}}} \quad (2)$$

where X_m is the mean concentration obtained, X_{ref} is the certified concentration value, SD is the standard deviation obtained in the analysis and $u_{(xref)}$ is the combined uncertainty of certificate value.
The calculation of the combined uncertainty is accomplished by the equation (3) where the expanded uncertainty was given by the certificate of the SRMs, and the k used was equal to 2 equivalents to 95 % confidence [21].

$$U_{exp} = u_c \times k \quad (3)$$

where u_c is the combined uncertainty, U_{exp} is the expanded uncertainty (obtained from the certificate) and k is a coverage factor.

According to Konieczka and Namiesnik criterion [20], the results is considered satisfactory when $|\text{Z-score}| \leq 2$, questionable when $2 < |\text{Z-score}| < 3$ and unsatisfactory for $|\text{Z-score}| \geq 3$.

The detection limit values were also calculated for the elements not detected in the analyses of AZ31 magnesium alloy. These detection limits were evaluated according to Currie [22] by applying the equation (4).

$$LDT = 3.29 \text{ X } \left(\frac{\sqrt{BG}}{LT}\right) \quad (4)$$

where LDT is counting rates related to detectable minimum concentration, BG is counting rate of background radiation or area under the peak and LT is counting time.

Using the LDT value, the detection limit in unit of concentration was calculated by comparative method using the equation (1).

3. RESULTS AND DISCUSSION

3.1 Quality Control of Results

In Table 2, results for Fe in SRM 58a Ferrosilicon and for Mg in SRM 1400 Bone Ash along with their respective certified values are presented.

Mg in SRM 1400 Bone Ash was calculated using the peak of 843.76 keV since the peak of 846.76 keV of ^{56}Mn could be considered negligible. The radioisotope ^{56}Mn in SRM 1400 Bone Ash was not detected and besides the peak of 1014.43 keV presented low counting rates and the accuracy using this peak was not good (Z-score = 5.0). As can be seen in Table 2, the results of Fe and Mg agree with certificate values presenting relative errors lower than 5.3%. They also presented good precision with relative standard deviations lower than 6.3%. The Z-score values obtained presented in Table 2 are |Z-score| < 2, indicating that the results are satisfactory.

Table 3 shows the determinations of the SRM 363 elements, along with the RSD and RE parameters.

Results obtained for SRM 363 Chromium – Vanadium Steel Modified presented in Table 3 show good precision and good agreement with the certified values for most of elements. The relative standard deviations varied from 3.7 to 13.9 % and the relative errors were lower than 15 % in most of the elements. The exceptions were for Co and Sb. For Co, the precision and the accuracy were not so good probably due to slow statistical counting rates obtained for the peak of ^{60}Co, since this element is present in low concentrations. For Sb, the accuracy of the results was not good, due to low statistical counting obtained for the peaks of ^{122}Sb and a spectral interference due the ^{76}As peak (559.10 keV).

In Figure 2, the Z-score values determined in the SRMs indicate the accuracy of the results obtained for most of the elements with |Z-score| ≤ 2.

3.2 Magnesium-based biomaterials analysis

In the Table 4, results of the elements determined in the pure magnesium sample are presented.

Table 2: Iron concentration in SRM 58a Ferrosilicon and magnesium concentration in SRM 1400 Bone Ash.

Element	SRM 58a	SRM 1400	
	Fe, %	Mg, % (843.76 keV)	Mg, % (1014.43 keV)
Certificate value [16-17]	25.239 ± 0.046	0.6840 ± 0.013	0.6840 ± 0.013
M ± SD (n=3)[a]	25.64 ± 0.63	0.648 ± 0.041	0.603 ± 0.010
RSD[b], %	2.5	6.3	1.6
RE[c], %	1.6	5.3	11.8
Z-score	0.6	-0.8	-5.0

a. arithmetic mean and standard deviation; b. relative standard deviation; c. relative error.

Table 3: Element concentrations obtained for SRM 363 Cr-V Steel Modified.

Element	n	Certificate [15]	M ± SD[a], %	RSD[b], %	RE[c], %
As, μg g^{-1}	6	100 ± 10	94.4 ± 6.8	4.1	4.1
Co, μg g^{-1}	5	480 ± 10	395 ± 55	13.9	17.7
Cr, %	6	1.31 ± 0.01	1.235 ± 0.056	4.5	5.7
Cu, %	4	0.10 ± 0.01	0.0871 ± 0.0057	6.5	12.6
Fe, %	3	94.40	92.1 ± 2.8	-	-
Mo, μg g^{-1}	5	280 ± 10	260 ± 31	12.0	7.2
Mn, %	3	1.50 ± 0.01	1.35 ± 0.15	10.8	9.9
Ni, %	4	0.30 ± 0.01	0.257 ± 0.010	3.7	14.2
Sb, μg g^{-1}	4	20 ± 10	16.01 ± 0.80	5.0	19.7
Ta, μg g^{-1}	4	530	490 ± 30	-	-
V, %	3	0.31 ± 0.01	0.306 ± 0.012	3.9	1.8
W, μg g^{-1}	3	460 ± 10	421 ± 39	9.3	8.5

a. arithmetic mean and standard deviation; b. relative standard deviation; c. relative error; -. not determined whereas this elements are not certified.

This Table shows that the pure magnesium sample presents a purity of (99.2 ± 2.7) % as can be seen in Table 4. The element impurities determined were Cr, Fe, Na and Zn at the level of mg g^{-1}, and the elements As, Cd, Co, In, La, Mn, Mo, Sb, V and W at the level μg g^{-1}.

The precision of these results were, generally good, with the RSD values varied from 2.8 to 14.8 % for most of the elements. The less precise results (RSD > 18.7 %) were obtained for Co, Fe, Sb and W determinations. For these elements the reproducibility of the results was not good probably due to low statistical counting rates or non homogeneity of the element in the sample.

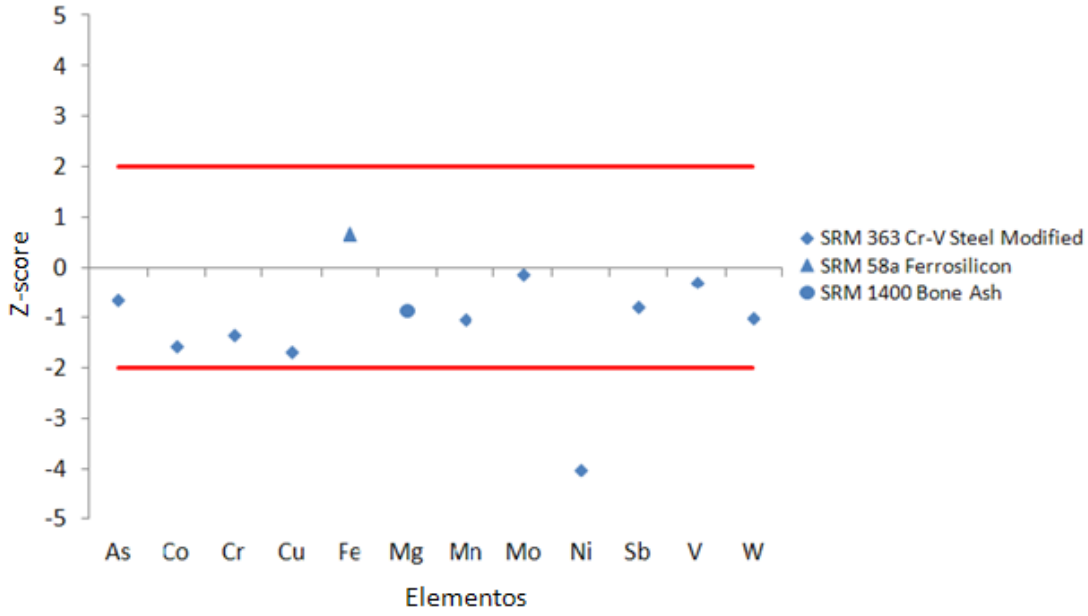

Figure 2: Z-score values obtained for the results obtained in the SRMs elements.

Table 4: Element concentrations obtained for pure magnesium sample.

Element	n[a]	M ± SD[b]	RSD[c], %
As, μg g^{-1}	4	0.222 ± 0.017	7.8
Cd, μg g^{-1}	3	35.6 ± 2.4	6.6
Co, μg g^{-1}	4	16.1 ± 3.2	20.1
Cr, mg g^{-1}	3	4.90 ± 0.72	14.8
Fe, mg g^{-1}	4	3.09 ± 0.70	22.7
In, μg g^{-1}	3	106 ± 12	11.3
La, μg g^{-1}	4	0.344 ± 0.043	12.6
Mg, %	4	99.2 ± 2.7	2.8
Mn, μg g^{-1}	5	698 ± 96	14.5
Mo, μg g^{-1}	3	12.3 ± 1.1	9.2
Na, mg g^{-1}	5	0.4756 ± 0.0060	12.4
Sb, μg g^{-1}	4	0.652 ± 0.187	28.7
V, μg g^{-1}	3	8.79 ± 0.06	7.3
W, μg g^{-1}	3	45.0 ± 8.4	18.7
Zn, mg g^{-1}	3	0.104 ± 0.012	11.7

a. number of repetitions; b. arithmetic mean and standard deviation; c. relative standard deviation.

In the Table 5 the results of determinations of the elements found in AZ31 alloy sample, as well as the detection limit values for the elements not detected (Cu, Fe and Ni).

Table 5: Concentrations obtained of the elements on AZ31 alloy.

Element	M ± SD[a]	RSD[b], %	Reference [23]
Al, %	3.06 ± 0.19	6.14	2.5 – 3.5
As, µg g^{-1}	2.30 ± 0.34	14.82	-
Cu, %	< 0.012	-	<0.05
Fe, %	< 0.095	-	<0.005
Mg, %	96.5 ± 4.2	4.4	Remainder
Mn, %	0.325 ± 0.013	3.9	0.2 – 1.0
Ni, %	< 0.037	-	<0.005
Na, µg g^{-1}	397 ± 32	8.1	-
Sb, ng g^{-1}	275 ± 56	20.4	-
La, ng g^{-1}	316 ± 16	5.2	-
Zn, %	1.009 ± 0.045	4.5	0.6 – 1.3

a. arithmetic mean and standard deviation from 2 to 4 determinations; b. relative standard deviation.

Concerning the results obtained from the AZ31 magnesium alloy analyses, Table 5 shows that Mg is present as majority element with concentration of (96.5 ± 4.2) % and concentrations of Al, Mn and Zn are within the values presented in the specification certificate [23]. The precision of the results were also good with relative standard deviation varying from 2.8 to 8.1 % for most of the elements.

The determination of Mg can suffer interference of Al due to the nuclear reaction: ^{27}Al (n,p) ^{27}Mg. However this interference could be considered negligible for the case of AZ31 sample due to low Al concentration (3.1 %) in relation to Mg (96%). Moreover the occurrence of this interference depends on the relationship between thermal and epithermal neutron fluxes.

It should be noted that the elements As, Na, Sb and La which are not presented in the specification certificate of AZ31 alloy were determined in this study. These elements presented in low concentrations at the levels from µg g^{-1} to ng g^{-1}. The elements Cu, Fe and Ni were not detected, so their limits values were evaluated and presented in Table 5.

The precision was not so good for Sb determination probably due the same reason cited on the pure magnesium analyses considering the significant presence of As in the sample leading the spectrum interference.

Among the elements determined in this study, As and Sb deserve consideration since they are toxic and they will dissolve in the human body. Arsenic has been shown to cause skin, lung, bladder, liver, and prostate and kidney cancers in humans [24]. Antimony is poisonous by inhalation and ingestion, and it is considered a carcinogen element, although the mechanisms of its toxicity are still unclear [25].

4. CONCLUSIONS

From the results obtained in this study it can be concluded that neutron activation analysis can be applied satisfactory in the determination of the element composition and impurities in

magnesium-based materials. The main limitations were the low statistical counting and the spectral interference mainly in Sb determination.

Results obtained in the analyses of standard reference materials demonstrated the accuracy and precision of the data obtained. The relative standard deviation of the elements were less than 14 %, which shows a good precision; and the relative errors were less than 15 % for most of the elements, presenting also good accuracy.

An analysis of the pure magnesium sample showed that its purity is (99.2 ± 2.7) % and the impurities, also determined by NAA indicated the viability of applying this technique for this kind of matrices due the great variety of the elements that can be determined.

Data obtained in the analysis of AZ31 magnesium alloy indicated a concentration of (96 ± 4) % of Mg and the alloying elements Al, Mn and Zn found were within the range presented in its specification certificate. Besides the following elements As, Na, Sb and La were determined as impurities in the alloy. Concerning As and Sb results, their determination are of interest since they considered toxic elements.

A contribution of the study is that toxic elements were detected and quantified by NAA technique. These results are of great importance since all the elements contained in the alloy will be dissolved in the human body. In future studies, solution extracts of magnesium-based materials will be analyzed.

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REFERENCES

1. B. D. Ratner, A. S. Hoffman, F. J Schoen, J. E Lemons, "*Biomaterials science - An introduction to materials in medicine"* Elsevier, Oxford, United Kingdom (2013) apud A.L.R. Pires, A.C.K Bierhalz, A.M. Moraes, "Biomateriais: tipos, aplicações e mercado*", Química Nova,* **38**, pp. 957-971 (2015).
2. N. Sezer, Z. Evis, S. M Kayhan, A. Tahmasebifar, M. Koc, "Review of magnesium-based biomaterials and their applications", *Journal of Magnesium and Alloys*, **6**, pp. 23-43 (2018).
3. B. A. Saw, "Corrosion resistance of magnesium alloy", *ASM Handbook*, **13a**, (2003).
4. X. N. Gu, S.S. Lo, X.M. Li, Y.B Fan, "Magnesium based degradable biomaterials: a review", *Frontiers of Material Sciences*, **8**, pp. 200-218 (2014).
5. O. Jung, R. Smeets, D. Porchetta, A. Kopp, C. Ptock, U.Müller, M. Heiland, M. Schwade, B. Behr, N. Kroeger, L. Kluwe, H. Hanken, P. Hartjen, "Optimized in vitro procedure for assessing the cytocompatibility of magnesium-based biomaterials", *Acta Biomaterialia*, (2015).
6. W. Ding, "Opportunities and challenges for the biodegradable magnesium alloys as next-generation biomaterials", *Regenerative Biomaterials*, **3**, pp. 79-86 (2016).

7. L. Tan, Q. Wang, X. Lin, P. Wan, G. Zhang, Q. Zhang, K. Yang, "Loss of mechanical properties in vivo and bone-implant interface strength of AZ31B magnesium alloy screws with Si-containing coating", Acta Biomaterialia, **10**, pp. 2333-2340 (2014).
8. X. Li, X. Liu, S. Wu, K. W .K Yeung, Y. Zheng, P. K Chu, "Design of magnesium alloys with controllable degradation for biomedical implants: from bulk to surface", *Acta Biomaterialia*, **45**, pp.2-30 (2016).
9. A. Pardo, M. C Merino, A. E. Coy, R. Arrabal, F. Viejo, E. Matykina, "Corrosion behavior of magnesium/aluminum alloys in 3.5% wt. NaCl", *Corrosion Science*, **50**, pp. 823-834 (2007).
10. E. Cincu, I. Manea, V. Manu, D. Barbos, O. Sima, I. Gustavsson, P. Vermaercke, N. Vajda, Zs. Molnar, H. Polkowska-Motrenko, "Comparative performance of INAA and other spectroscopy techniques in the elemental analysis of stainless steel materials", *Journal of Radioanalytical and Nuclear Chemistry*, **274**, pp. 199-205 (2007).
11. I. Manea, E. Cincu, L. Craciun, I.L Cazan, V. Manu, D. Barbos, A. Cocis, "Application of the INAA technique for elemental analysis of metallic biomaterials used in dentistry", *Applied Radiation and Isotopes*, **67**, p. 2133-2136 (2009).
12. A. D. Shinde, R. Acharya, A.V.R Reddy, "Analysis of zirconium and nickel based alloys and zirconium oxides by relative and internal monostandard neutron activation analysis Methods", *Nuclear Engineering and Technology*, **49**, pp. 562-568 (2017).
13. L. A. Hamidatou, "Overview of Neutron Activation Analysis". *IntechOpen* (2019).
14. W. D. Ehmann, *Radiochemistry and Nuclear Methods of Analysis*, John Wiley & Sons, Inc. (1999)
15. NIST. National Institute of Standards and Technology. Certificate of analysis. Standard Reference Material 363 Chromium Vanadium Modified, pp. 1-3 (2012).
16. NIST. National Institute of Standards and Technology Certificate of analysis. Standard Reference Material 1400 Bone Ash, pp.1-3 (1992).
17. NIST. National Institute of Standards and Technology. Certificate of analysis. Standard Reference Material 58a Ferrosilicon, pp. 1-4 (2009).
18. IAEA – TEC DOC 564 Practical Aspects of Operating a Neutron Activation Analysis Laboratory, IAEA, Vienne (1990).
19. D. De Soete, R. Gijbels, J. Hoste, *Neutron Activation Analysis*, Wiley-Interscience, London, United Kingdom, 1972.
20. P. Konieczka, J. Namiesnik, *Quality Assurance and Quality Control in the Analytical Chemical Laboratory: a practical approach*, CRC Press, Florida, USA (2009).
21. NAMAS. National Measurements Accreditation Service. NIS 3003. United Kingdom, 8ª Edition (1995).
22. L. A. Currie, "International recommendations offered on analytical detection and quantification concepts and nomenclature", *Analytica Chimica Acta*, **391**, pp. 127-134 (1999).
23. Alfa Aesar by Thermo Fisher Scientific. 44009 Magnesium Aluminum Zinc foil, https://www.alfa.com/pt/catalog/044009/&gt, (2018).
24. M. Costa, "Review of arsenic toxicity, speciation and polyadenylation of canonical histones", *Toxicology and Applied Pharmacology*, **375,** pp 1-4 (2019).
25. C. Hansell, "All manner of antimony", *Nature Chemistry*, **7**, pp.8 (2015).