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Analyses of magnesium-based alloys by nuclear techniques

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ABSTRACT

Magnesium-based alloys have been proposed for use in temporary biomaterials in the applications that request their biocompatibility and degradability. Analyses of these alloys are of great interest to verify if their element composition is within the product specification and also to evaluate the impurities that may cause toxic effects to the human health or influence in their corrosion processes. In this study, nuclear techniques of neutron activation analysis (NAA) and wavelength dispersive X ray fluorescence spectrometry (WD XRFS) were applied in the analyses of two magnesium-based alloys: commercially pure magnesium (CP-Mg) and AZ31 alloy. The NAA procedure consisted of irradiation aliquots of sample and synthetic element standards followed by measurements using a HGe detector and the WD XFRS was carried out using the Model RIX 3000 X-ray spectrometer. In the CP-Mg sample several element impurities were quantified. In the AZ31 alloy, the alloying element mass fractions were within the product specification and the impurities of As, La, Na and Sb were also quantified. Nickel and sulfur were quantified only by WD XFRS. The Horwitz method was a good parameter to evaluate the repeatability of the results in Al, Mg, Mn and Zn determinations. In conclusion, the results indicated the viability of using NAA and WD XFRS in the analyses of magnesium-based materials mainly due its multielement determinations, precision of the results, quantification of elements in a wide range of mass fractions and the lack of need for sample dissolution.

Keywords: **magnesium-based alloys, nuclear analytical techniques, biomaterials.**

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1. INTRODUCTION

The application of reliable techniques in the analyses of alloys used as biomaterials is of great importance once the element composition and their impurities can influence the corrosion and consequently on the patient’s health. Biomaterials should not cause adverse effects such as allergy, inflammation or toxicity either immediately after surgery or under post operative conditions [1]. Besides the presence of impurities in metallic biomaterials, for instance, may initiate localized corrosion in relation to a grain causing early failure [2].

Magnesium and its alloys have been gaining great interest in medical devices which request biocompatibility and degradability [3-4] such as orthopedic protheses and cardiovascular *stents*. However, high corrosion rates are the main limitation of using these alloys, impairing the functioning of the material once they might corrode before the cell healing [5].

Chemical analyses can provide a consistent basis for equitable treatment of producer and consumer in raw materials and finished products. Moreover, they are critical to industrial quality control, as well as for assessing the performance and assuring the reliability of materials in service [6]. In this way, biomaterial analysis is of interest not only for the health area but for the industries which produce them.

Therefore, a chemical analysis is necessary to identify unwanted or unexpected impurities and whether the element concentrations are within their specification concentration ranges [7]. Besides, in the case of magnesium-based materials, publications about their element determinations are very scarce.

Several analytical techniques have been used for element determination in metallic alloys such as atomic absorption spectrometry (AAS) [8], X-ray fluorescence spectrometry (XRFS) [9], UV-vis spectrophotometry [10], inductively couple plasma by atomic emission spectroscopy (ICP-AES) [11], inductively couple plasma by optical emission spectrometry (ICP-OES) [12], and neutron activation analysis (NAA) [13].

Among these techniques, NAA and wavelength dispersive X ray fluorescence spectrometry (WD XRFS) were used in this study due to their advantages of the capability of a multi-element analysis for a wide range of mass fractions of elements without sample dissolution. The alloy dissolution is not always an easy task and also it requires the use of chemical reagents that can often contaminate the sample. The WD XFRS is also considered an appropriate analytical tool for determining element compositions due to a strong standardless quantification capability [14]. On the other hand, NAA allows to obtaining accurate results for major and trace elements when compared with those obtained by AAS [15].

The objective of this study was to analyze magnesium-based materials (commercially pure magnesium - CP-Mg) and AZ31 alloy applying NAA and WD XRFS.

2. MATERIALS AND METHODS

2.1. Materials

The Mg-based materials analyzed were commercially pure magnesium (CP-Mg) and AZ31 magnesium alloy. The CP-Mg was acquired in ingot form and the AZ31 Mg alloy was in sheet form in the dimensions of 30 x 30 x 0.1 cm.

The preparation of these materials for NAA is described in the previous publication [16]. For WD XFRS analyses the samples were cut using a mechanical guillotine in (15 x 15 x 1) mm dimensions. Then, these samples were cleaned under ultrasonic shaking for 15 min in each of the reagents: acetone PA, ethyl alcohol PA and purified water. To obtain smooth and uniform surfaces, the samples were also sanded using silicon carbide sandpaper successively with different grain sizes.

2.2. Neutron activation analysis procedure

For NAA about 50 mg of each sample were weighed in polyethylene envelopes for irradiation. To prepare synthetic element standards, first single and multielement solutions were obtained using certified standard solutions of elements purchased by Spex CertiPrep USA. Then adequate aliquots of these solutions were pipetted onto sheets of Whatman N° 40 filter paper. These filter sheets were dried at room temperature inside a desiccator and then placed into clean polyethylene involucres which were sealed.

The analyses were carried out at the Neutron Activation Analysis Laboratory of the Research Reactor Center (CERPq) IPEN-CNEN/SP by irradiation at the IEA-R1 nuclear reactor. Synthetic element standards were irradiated together with the samples for a short period (10 s under a thermal neutron flux of 1.9 x 10^{12} n cm^{-2} s^{-1}) and for long period (8 h under a thermal neutron flux of 4.5 x 10^{12} n cm^{-2} s^{-1}).

After adequate decay times, the element standards and samples were measured using a Model GC 2018 Hyperpure Germanium detector coupled to a Digital Spectrum Analyzer (DSA 1000). Genie 2000 Version 3.1 software from Canberra was used to acquire and process the data of gamma-ray spectra. The gamma activity measurements were carried out in different decay times in order to avoid the problem of interference in the analysis. The radionuclides (half-life ; gamma ray 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), ^{187}W (23.9 h; 479.57 keV), ^{52}V (3.75 min; 1434.08 keV), ^{65}Zn (243.9 d; 1115.55 keV) and ^{29}Al (6.56 min ; 1273.36 keV) for Si determination. The element mass fractions were calculated by comparative method in Equation (1) [17].

$$C_s = \frac{m_{st}.A_s.e^{(0.693(ts-tst))/\mathrm{t}_{1/2}}}{M_s.A_{st}} \tag{1}$$

where C_s is the mass fraction in the sample; m_{st} is the mass of the element in the standard; A_s and A_{st} are counting rates of the radionuclide in the sample and in the standard, respectively; ts and tst are decay times 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.

The epithermal neutron activation analysis (ENAA) was also carried out for Si determination by measuring ^{29}Al formed in the nuclear reaction ^{29}Si (n,p) ^{29}Al. The ENAA procedure consisted of irradiating sample and Si standard of powder metallic silicon weighted in polyethylene envelopes, for short irradiation of 60 s. The sample and Si standard were placed in a Cd capsule and irradiated in a position nuclear reactor with thermal and epithermal neutron flux of about 1.9 x

10^{12} n cm^{-2} s^{-1} and 5.43 x 10^{10} n cm^{-2} s^{-1}, respectively. Results of analytical quality control obtained in the NAA of alloys are published in a previous publication [16].

2.3. Wavelength dispersive X-ray fluorescence spectrometry procedure

The analysis were carried out using a RIGAKU Co (Tokyo, Japan) wavelength dispersive X-ray fluorescence spectrometer (WDXRF), model RIX 3000 with a Rh-anode X-ray tube, a 75 µm Be window, a 60 kV maximum acceleration voltage generator, a NaI(Tl) scintillation detector and a gas-flow proportional counter. The 2-theta scan model was applied data acquisition. The Compton and fundamental parameters (FP) method were applied for correction of the absorption/excitation effects [18]. The parameters such as excitation, emission line, divergence slit, diffracting crystal, type of detector, scan counting time, and Bragg's positions are shown in Table 1.

Table 1: Measurement conditions for WD XRFS – Excitation : 50 kV x 50 mA.

Elements	**Emission line**	**Divergence slit (µm)**	**Diffracting crystal**	**Detector**	**Step (°) / Time (s)**	**Bragg's positions (°)**
Na	Na-Kα	560	TAP	FPC	0.05 / 1.0	52.000-58.000
Mg	Mg–Kα	560	TAP	FPC	0.05 / 1.0	42.000-48.000
Al	Al-Kα	560	PET	FPC	0.05 / 1.0	140.000-147.000
Si	Si-Kα	560	PET	FPC	0.05 /0.4	106.000-112.000
P	P-Kα	560	Ge	FPC	0.05/0.4	138.000-144.000
S	S-Kα	560	Ge	FPC	0.05/0.4	108.000-114.000
Cl	Cl-Kα	160	Ge	FPC	0.05/1.0	90.000-96.000
K	K-Kα	560	Ge	FPC	0.05/0.4	60.000-64.000
Ti-U	Kα	560	LiF(200)	SC	0.02/0.2	5.000-90.000
Rh-C	Kα	560	LiF(200)	SC	0.02/0.2	17.000-18.000

TAP: thallium acid phtalate, PET: pentaerythritol, LiF: lithium fluoride, Ge: germanium, SC: scintillation detector, NaI(Tl): FPC gas-flow proportional counter, Rh-C: rhodium Compton.

The methodology was validated in terms of precision and accuracy through statistical tests suggested by INMETRO's document DOQ-CGCRE-008 [19]. The data were obtained for 7 measurements of a sample in pellet form produced with high purity compounds ($MgCl_2$, Al_2O_3 and ZnO – Merck) according to AZ31 alloy specification (96% Mg, 3% Al and 1% Zn). The Mg, Al, Zn and Rh-Compton spectrum were adjusted by Oringin-Pro8 software using Lorentz nonlinear curve fit function for the area. The results AZ31 alloy and Mg sample analyses were calculated by Equation 2.

$$C = \frac{AS * \frac{ACS}{ACP} * tP}{AP} \quad (2)$$

where, *C* is the mass fraction obtained, *AS* is area of unknown sample in the peak position; *ACS* is area of unknown sample in the Compton position; *ACP* is area of known sample (pellet) in the Compton position; *tP* is amount of known sample (pellet) and *AP* is area of known sample (pellet) in the peak position.

2.4. Precision evaluation by HORRAT values

The precision was evaluated through the relative standard deviation (%RSD) and the acceptability was verified using the equation of Horwitz, in which the HorRat's (HO_R) values fit more accordingly by Equation 3 [19].

$$HO_R = \frac{RSD\%_{experiment}}{RSD\%_{Horwitz}} \quad (3)$$

where HO_R is the HorRat's value, $RSD\%_{experiment}$ is the relative standard deviation obtained in the analysis and the $RSD\%_{Horwitz}$ is the relative standard deviation provide by Horwitz method.

3. RESULTS AND DISCUSSION

The following elements were quantified in the magnesium-based material: As, Cd, Co, Cr, In, La, Na, Sb, Si, V e W by NNA thecnic; Fe, Mg, Mn and Zn by NNA and WDXRFS thecnics; S only WDXRFS thecnic.

Table 2 presents mass fractions elements in the commercially pure magnesium sample (CP-Mg) quantified by NNA and WDXRFS and reference values. Furthermore, RSD (%) and HO_R calculated values for NAA and WDXRFS techniques.

The results showed NNA and WDXRFS techniques are statistically equal for Mg quantification because calculated value for comparison of means using Z-test (z = 0.26) is lower than critical value (z = 1 .96) for 0.05 significance level. In addition, they agree with reference value since percentage relative error (RE%) for NNA and WDXRFS were (0.6%) and (0.1%), respectively. The precision is also satisfactory because HOr values are < 2.0 for both techniques. The Mn element quantification by WDXRFS was a lower less than reference value. One hypothesis can it be to inefficiency FP Method for absorption/excitation effects corrections. However, method it is sufficient to ensure Mn in sample. The mass fractions for Fe and Zn are enough for both techniques. The NNA technique is more sensitive than WDXRFS because it quantified a significance number impurities with satisfactory precision (HOr < 2.0), except for Co, Sb and W (Hor; 2.5, 2.6, 3.1).

Table 2: Element mass fractions in commercially pure magnesium sample (CP-Mg) by NAA and WD XRFS.

Elements	**NAA**			**WDXRFS**			**Reference**
	M ± SD	**RSD (%)**	**HOR values**	**M ± SD**	**RSD (%)**	**HOR values**	**[21]**
As, µg g^{-1}	0.222 ± 0.017	7.7	0.7	ND	-	-	80
Cd, µg g^{-1}	35.6 ± 2.4	6.7	1.0	ND	-	-	-
Co, µg g^{-1}	16.1 ± 3.2	19.9	2.5	ND	-	-	-
Cr, mg g^{-1}	4.90 ± 0.72	14.7	1.9	DN	-	-	-
Fe, mg g^{-1}	3.09 ± 0.70	22.7	4.5	<50	-	-	-
In, µg g^{-1}	106 ± 12	11.3	1.9	ND	-	-	-
La, µg g^{-1}	0.344 ± 0.043	12.5	1.1	ND	-	-	-
Mg, %	99.2 ± 2.7	2.7	1.4	99.9 ± 0.1	0.1	0.02	99.82
Mn, µg g^{-1}	698 ± 96	13.8	2.3	170 ± 20	11.8	1.5	480
Mo, µg g^{-1}	12.3 ± 1.1	8.9	1.2	ND	-	-	-
Na, mg g^{-1}	0.498 ± 0.036	7.2	1.8	ND	-	-	-
S, %	-	-		0.011 ± 0.001	10	1.3	-
Sb, µg g^{-1}	0.652 ± 0.187	28.7	2.6	ND	-	-	-
Si, µg g^{-1}	<14	-		ND	-	-	330
V, µg g^{-1}	8.79 ± 0.06	0.7	0.1	ND	-	-	-
W, µg g^{-1}	45.0 ± 8.4	18.7	3.1	ND	-	-	-
Zn, mg g^{-1}	0.104 ± 0.012	11.5	1.4	<50	-	-	70

M±SD ≡ arithmetic mean and standard deviation; RSD(%) ≡. percentage relative standard deviation; HOR ≡ relative standard deviation acceptability criterion; ND ≡ not detected;

The following elements were quantified in the AZ31 alloy sample: As, Cu, Fe, La, Na, Sb and Si by NNA thecnic; Al, Mg, Mn Ni, S and Zn by NNA and WDXRFS thecnics; S only WDXRFS thecnic. Table 3 presents mass fractions elements in the AZ31 alloy sample (CP-Mg) quantified by NNA and WDXRFS and reference values. Furthermore, RSD (%) and HO$_R$ calculated values for NAA and WDXRFS techniques.

Table 3: Element mass fractions obtained in AZ31 alloy sample by NAA and WD XRFS.

Elements	**NAA**			**WDXRFS**			**Reference**
	M ± SD	**RSD (%)**	**HO$_R$ values**	**M ± SD**	**RSD (%)**	**HO$_R$ values**	**[21]**
Al, %	3.06 ± 0.19	6.2	2.0	2.7 ± 0.1	3.7	1.2	2.5 – 3.5
As, µg g^{-1}	2.30 ± 0.34	14.8	4.9	ND	-	-	-
Cu, %	< 0.012	-		ND	-	-	<0.05
Fe, %	< 0.095	-		ND	-	-	<0.005
La, ng g^{-1}	316 ± 16	5.1	0.5	DN	-	-	-
Mg, %	96.5 ± 4.2	4.3	2.0	93.7 ± 0.1	0.1	0.1	94 – 96
Mn, %	0.325 ± 0.013	4.0	1.0	1.0 ± 0.1	10.0	2.5	0.2 – 1.0
Ni, %	< 0.037	-		0.020 ± 0.002	10.0	1.7	<0.005
Na, µg g^{-1}	397 ± 32	8.1	2.0	ND	-	-	-
S, %	ND	-		0.06 ± 0.01	16.7	2.8	-
Sb, ng g^{-1}	275 ± 56	20.4	1.0	ND	-	-	-
Si, %	< 4.36	-		ND	-	-	<0.05
Zn, %	1.009 ± 0.045	4.5	1.1	1.3 ± 0.2	6.5	1.6	0.6 – 1.3

M±SD ≡ arithmetic mean and standard deviation; RSD(%) ≡. percentage relative standard deviation; HO$_R$ ≡ relative standard deviation acceptability criterion; ND ≡ not detected;

The results showed NNA and WDXRFS techniques are statistically equal for Mg quantification because calculated value for comparison of means using Z-test ($z = 0.67$) is lower than critical value ($z = 1\ .96$) for 0.05 significance level. In addition, they agree with reference value. The precision is also satisfactory because HOr values by NNA = 2.0 and WDXRFS <2.0. The Mn element quantification by WDXRFS was a lower less than reference value. One hypothesis can it be to inefficiency FP Method for absorption/excitation effects corrections. However, method it is sufficient to ensure Mn in sample. For Al, Cu, Mn and Zn, the results obtained are within the values presented in its specification document. Moreover, As, La, Na and Sb not presented in the specification, were quantified in this study and they could be considered as impurities. Element Si was not detected and detection limit value was calculated. By using WD XRFS technique, six elements were determined in the AZ31 alloy and the elements S and Ni could be quantified only by this technique.

Results presented in Table 2 and 3 show the determinations of several elements by NAA and WD XRFS which indicates the possibility of applying nuclear techniques to detect the presence of undesired and unexpected elements that can lead the formation of secondary phases in the alloy, which can accelerate or inhibit the degradation rate [23]. Once these element impurities are identified, further studies can be carried out to assess the effect of their presence on the toxicity and corrosion of alloys applied as biomaterial.

4. CONCLUSION

Nuclear analytical techniques applied in analyses of magnesium-based materials demonstrated the application of NAA and WD XRFS in the determination of alloying elements informed in the product specification of the alloy as well as impurities.

The results obtained confirmed the feasibility of applying these nuclear techniques in the analyses of alloys, mainly due to their character of multielemental analysis, precision of the results, high sensitivity and the possibility of purely intrumental analysis without sample digestion.

From the results obtained, it can also be concluded that NAA and WD XRFS may contribute to the improvement of the production of magnesium-based alloys for use as biomaterials.

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