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Determination of chemical elements in magnesium-based materials by neutron activation analysis

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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.

Keywords: **biomaterials, magnesium alloys, neutron activation analysis, chemical elements, impurities.**

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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, in other words, 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 [5-7].

However, rapid degradation rates in physiological environments constitute the main limitation for these alloys essentially in degradation cases before cell healing [8-10]. 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 [11]. Hence, an adequate chemical characterization of these materials is indispensable in a corrosion study. The neutron activation analysis (NAA) is an instrumental technique used to determine the elemental composition of metal alloys [12-14] and was the method used to carry out the analysis.

According to Hamidatou 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 [15]. 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 [16-18]. In the case of alloys, they often present difficulty of dissolutioin due to the higher resistance to attack with acids when compared with other matrices that can be easily obtained in fine powder form.

The objective of this study was to analyze magnesium-based materials (pure magnesium and AZ31 magnesium 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

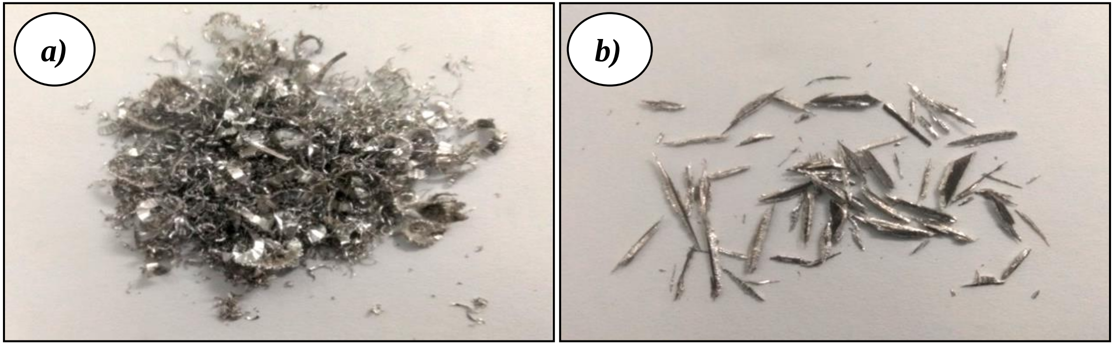
Magnesium alloys are known for being the lightest structural alloys and they are produced by mixing Mg with other metallic elements such as Al, Zn, Si, Co, Zr and rare earth elements to improve their physical properties. Due to its favorable properties of low specific gravity and high strength-to-weight ratio, these alloys of Mg present wide applications in the automodive, aerospace, eletronics and biomedical devices [19].

Materials used in this study were magnesium-based materials and standard reference materials. The magnesium-based materials analyzed were: pure magnesium and magnesium alloy coded AZ31 with about of 96 % Mg, 3 % Al and 1 % Zn. The pure magnesium sample was acquired in ingot form and the magnesium alloy in sheet form with the dimensions of 30 x 30 cm^2 and 1 mm thickness.

Preparation of these materials for the analyses was carried out by cutting them in the form of filings 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 p.a. Then, the acetone was removed and the samples were rinsed in a beaker with purified water (Millipore system), in which the filings stayed immersed for about two hours. The filings were separated from the liquid by filtration on filter paper. This filter paper with the samples was placed in a Petri dish for drying inside a laminar flow cabinet [20].

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

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



The standard reference materials (SRMs) from the National Institute of Standards and Technology (NIST) were analyzed in order to evaluate the quality control of the results. These SRMs were: SRM 363 Chromium-Vanadium Steel Modified [21], SRM 1400 Bone Ash [22] and SRM 58a Ferrosilicon [23]. 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 determined to correct the Mg results. The moistures for metallic standard reference materials were considered negligible.

2.2. Neutron activation analysis procedure

For preparing synthetic element standards, first single and multielement solutions were obtained using certified standard solutions of elements purchased by Spex CertiPrep USA [24]. 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 [25]. 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 involucres which were heat sealed [26, 27].

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	10004.0	1000.40
S6	As Cu Mo Sb	30.00 1999.92 60.18 12.03	1.50 100.0 3.01 0.60
L6	Cd Co La	200.07 3.00 12.00	10.00 0.15 0.60
Fe8	Fe	10009.00	500.45
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

For neutron activation analysis, 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. Two separate irradiations were used to determine elements having short and long-lived irradiations.

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 research 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 [28]. 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) [29].

The element concentrations were calculated by comparative method using the equation (1) [30].

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

where C_s is the 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 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.

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 were calculated using equation (2) in order to evaluate the accuracy of the results in the analyses of the standard reference materials [31].

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

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 certified value.

The calculation of the combined uncertainty is accomplished by the equation (3) where the expanded uncertainty is presented in the certificates of the SRMs, and the k used was equal to 2 for 95 % confidence level [32].

$$U_{exp} = u_c \text{ x } k \qquad (3)$$

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 the results is considered satisfactory when $|\text{Z-score}| \leq 2$, questionable when $2 < |\text{Z-score}| < 3$ and unsatisfactory for $|\text{Z-score}| \geq 3$ [31].

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 by applying the equation (4) [33].

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

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.

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 [22,23]	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

M ± SD = arithmetic mean and standard deviation; n = number of determination; RSD = relative standard deviation; RE = relative error.

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 satisfactory (Z-score = - 5.0).

Although Mg is presenting a concentration relatively high of (0.6840 ± 0.013) %, this element does not present very favorable characteristics for NAA. That is, the target isotope ^{26}Mg has an isotopic abundance of 11.01 % and the thermal neutron cross-section and integral ressonance of

0.0372 and 0.024 barns, respectively. So that is the reason of the peak of 1014.4 keV (^{27}Mg) presents low counting rates.

On the other hand, as still can be seen in Table 2, the results of Fe and Mg agree with certified 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 results of elements along with the relative standard deviation and relative error parameters for SRM 363 Chromium-Vanadium Steel Modified.

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

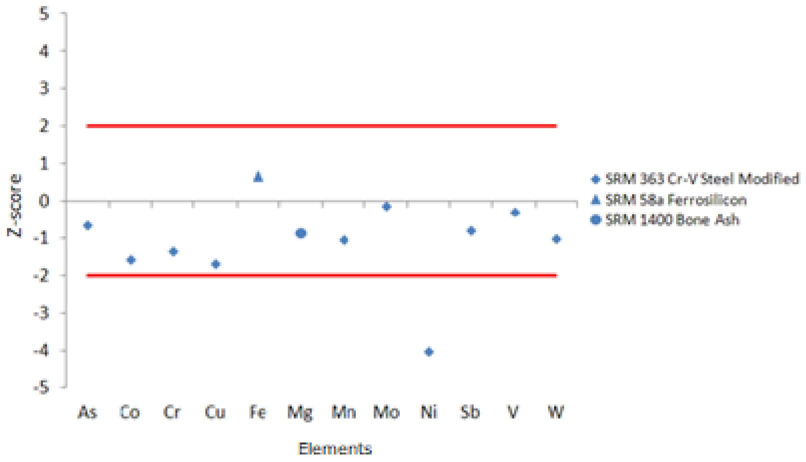
Elements	**This study**				**Certificate value [21]**
	n	**M ± SD**	**RSD, %**	**RE, %**	
As, µg g^{-1}	6	94.4 ± 6.8	7.2	5.6	100 ± 10
Co, µg g^{-1}	5	395 ± 55	13.9	17.7	480 ± 10
Cr, %	6	1.235 ± 0.056	4.5	5.7	1.31 ± 0.01
Cu, %	4	0.0871 ± 0.0057	6.5	12.6	0.10 ± 0.01
Fe, %	3	92.1 ± 2.8	3.0	*	(94.4)**
Mo, µg g^{-1}	5	260 ± 31	12.0	7.2	280 ± 10
Mn, %	3	1.35 ± 0.15	10.8	9.9	1.50 ± 0.01
Ni, %	4	0.257 ± 0.010	3.7	14.2	0.30 ± 0.01
Sb, µg g^{-1}	4	16.01 ± 0.80	5.0	19.7	20 ± 10
Ta, µg g^{-1}	4	490 ± 30	6.1	*	(530)**
V, %	3	0.306 ± 0.012	3.9	1.8	0.31 ± 0.01
W, µg g^{-1}	3	421 ± 39	9.3	8.5	460 ± 10

n = number of determinations; M ± SD = arithmetic mean and standard deviation; RSD = relative standard deviation; RE = relative error; * not determined; ** numbers in parenthesis are informative values.

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 3.0 to 13.9 % and the relative errors were lower than 15 % for most of elements. The exceptions were for Co and Sb. For Co, the precision and the accuracy were not so satisfactory 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 satisfactory, due to low statistical counting obtained for the peak of ^{122}Sb (564.24 keV)and spectral interference of the peak (559.10 keV) of ^{76}As.

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

Figure 2: *Z-score values obtained for the elements determined in the standard reference materials(SRMs)*



3.2 Magnesium-based biomaterials analyses

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

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

Concerning the results obtained for 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 [34]. The precision of the results were also good with relative standard deviation varying from 2.8 to 8.1 % for most of the elements.

Table 4: Element concentrations obtained for pure magnesium sample

Element	n	M ± SD	RSD, %
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

n = number of determinations; M ± SD = arithmetic mean and standard deviation; RSD = relative standard deviation.

Table 5: Element concentrations obtained in AZ31 magnesium alloy**.**

Element	M ± SD	RSD, %	Reference [34]
Al, %	3.06 ± 0.19	6.1	2.5 – 3.5
As, µg g^{-1}	2.30 ± 0.34	14.8	*
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

M ± SD = arithmetic mean and standard deviation from 2 to 4 determinations; RSD = relative standard deviation; * - indicates not determined or not presented in the indicated reference.

The determination of Mg can present 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 alloy 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 detection 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 analysis of the presence of As that causes spectral interference.

Among the elements determined in this study, As and Sb deserve consideration since they are toxic and they can dissolve in the human body.

According to Schuhmacher-Wolz et al. who reviewed toxicological and epidemiological data on As, this element can cause carcinogenic effects mainly of skin, lung and urinary bladder tumors, as well as non-cancerous effects causing the development of cognitive and cardiovascular diseases and reproductive effects [35].

In the case of Sb, its toxicity due to occupational exposure to this element can cause respiratory irritation, pneumoconiosis, gastrointestinal symptoms and Sb spots on the skin. When this element is used in theraphy it can cause its side effects of cardiotoxicity and pancreatitis [36].

4. CONCLUSION

From the results obtained in this study it can be concluded that neutron activation analysis can be applied in the determination of element composition and impurities in magnesium-based materials.

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 and Na (at the level of µg g^{-1}), Sb and La (at the level of ng g^{-1}) were determined. For pure magnesium sample a purity of (99.2 ± 2.7) %

of Mg and element impurities of Cd, Cr, Co, Fe, In, La, Mn, Mo, Na, Sb, W and Zn were determined.

Analyses of standard reference materials demonstrated the accurancy and reproductibility of the results obtained for most of the elements determined.

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