Chemical Characterization of Highly Pure Magnesium Metal by RF GD-OES

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Abstract

This present paper outlines a newly developed Radio Frequency Glow Discharge Optical Emission Spectrometer (RF GD-OES) method for the quantification of various impurities in highly pure magnesium metal. A comprehensive optimization process was undertaken to establish ideal glow discharge plasma operating conditions, encompassing parameters such as the forward power supplied to the GD plasma, the argon gas pressure within the plasma chamber, pre-integration time, and integration time. This optimization aimed to achieve linear calibration curves, optimal precision and accuracy. Notably, the internal standard calibration approach yielded more accurate and reliable results when contrasted with direct calibration. The method has been validated using Certified Reference Materials (CRMs) procured from MBH & NCS, and further corroborated by comparative analysis with the Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) technique. In the developed method, it is found that % RSD is less than 5% using internal standard calibration approach.

Key words: Magnesium, GD-OES, PHWR, Zirconium metal, Critical impurities

1. Introduction

Nuclear Fuel Complex (NFC), as an industrial division of the Department of Atomic Energy (DAE), is tasked with the manufacturing and supply of nuclear fuel assemblies and reactor core structural components for all pressurized heavy water reactors (PHWRs) and boiling water reactors (BWRs) in India. Additionally, NFC provides sub-assemblies for the country's first Prototype Fast Breeder Reactor (PFBR), primarily for electricity generation. Zirconium alloys are extensively utilized in the fabrication of various reactor core components, including fuel clad and calandria tubes, particularly in water-cooled nuclear

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power reactors such as BWRs and PHWRs. This widespread use is attributed to their favorable properties, which include a low neutron absorption cross-section, optimal mechanical properties, robust corrosion resistance in high-temperature aqueous environments, and resistance to radiation damage. Reactor-grade Zirconium metal (RG Zr metal) serves as the starting material for producing various Zirconium alloys (Zircaloys) and is synthesized by the well-established Kroll's reduction process, as shown below.

$$ZrCl_4\ (v) + 2\ Mg\ (l) \xrightarrow{900\ ^oC} Zr\ (s) + 2\ MgCl_2\ (l) \quad \Delta H = -78.6\ Kcal/mole$$ [1]

Essential nuclear reactor core components like fuel clad tubes, pressure tubes, calandria tubes are manufactured using different grades of Zircaloys [2, 3]. In view of applications in reactor, stringent specifications are laid down for RG Zr metal and to meet the desired purpose, it is essential to monitor the quality of all input materials used for making Zircaloys which includes RG Zirconium metal. As mentioned above, Magnesium (Mg) metal is used in the process of producing RG Zirconium metal and therefore it becomes essential to monitor the quality of Mg metal as well with respect to impurities Al, Cu, Fe, Mn, Ni, Si and Ti. The self-imposed specifications listed for Magnesium metal which are laid down as per the production requirements at NFC are given in Table 1**.**

Table 1 Specifications of Magnesium metal

Element	Max allowable limit (%)
Al	0.0040
Cu	0.0030
Fe	0.0050
Mn	0.0070
N	0.0020
Ni	0.0010
Si	0.0100
Ti	0.0025

Different analytical techniques like Flame-AAS [4], DC-Arc based Optical Emission Spectrometry (OES) [5], Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [6,7], Glow Discharge Mass Spectrometry (GD-MS) [8] and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) [9,10] etc., are cited in literature for qualifying Mg metal

for further use. The inherent limitations of all these mentioned methods make them less suitable options for an industrial laboratory with substantial analytical workload demands. DC-Arc based OES method involves cumbersome sample preparation procedures and also generates NOx fumes. With its low sensitivity measurements, Flame-AAS does not fit into requirement, as the elements are to be quantified at trace levels. Similarly, ICP-OES requires dissolution of samples and generates NOx fumes during this process. The dissolution leads to generation of liquid analytical waste. Conventional analytical methods often prove impractical for industrial laboratories facing high sample throughput and stringent waste disposal regulations. Specifically, the liquid analytical waste generated during sample treatment poses a significant disposal challenge, especially from a nuclear industry. To address these limitations, a systematic study was conducted to develop a direct solid-based analytical method for quantifying impurity elements (Al, Cu, Fe, Mn, Ni, Si, and Ti) in highly pure Magnesium metal using Radio Frequency Glow Discharge Optical Emission Spectrometry (RF GD-OES). ICP-OES method is widely used method for the analysis of impurities in Magnesium metal. However, the factors such as generation of NOx fumes during dissolution, generation of liquid analytical waste limits its applications, especially for an industrial laboratory attached to a nuclear industry. Disposal of liquid analytical waste from nuclear industry is a difficult task and also involves laborious procedures. Further, the disposal becomes more complex, when high volume liquid analytical waste is generated. In general, the volume is high for an industrial laboratory attached to the production plant, as it encounters large analytical load on regular basis for chemical clearance. ICP-OES being widely used method (including in our laboratory), the same is taken for comparison of the analytical data and method validation in the present case. We have developed RF GDOES method to address disposal problem and also through-put. With direct solid sample analysis capability, RF GDOES scores over ICP-OES method especially for an industrial lab attached to production plants. It has distinct advantage of eliminating the generation of liquid analytical waste and there-by its disposal problem as well. Also, has high through-put compared to ICP-OES method, as it doesn't involve time consuming sample dissolution step.

2. Experimental

2.1 Sample Preparation for GD-OES analysis

The existing GD-OES instrument, designed for vertical sample mounting, operates under argon atmosphere. Maintaining this environment is critical, as atmospheric air leakage into

the glow discharge zone can extinguish the plasma. This design necessitates samples with flat, smooth surfaces to prevent such leakage, making the analysis of samples with rough or irregular finishes extremely challenging. Additionally, achieving proper power matching was observed to be difficult with rough surfaced samples. Therefore, all samples required polishing using 200-grit paper to ensure surface flatness to obtain precise analytical results.

2.2 Instrument Details

Radio Frequency Glow Discharge Optical Emission Spectrometer (GD-OES) (GD-PROFILER HR model from Horiba Jobin Yvon, France) has been utilized in the present study. This instrument operates with an RF generator frequency of 13.56 MHz, delivering forward power up to 100 W to maintain argon plasma at 900 Pa. Its analytical capabilities span a wavelength range of 120 nm to 600 nm, facilitated by High Dynamic Detectors (HDD). The system incorporates both a monochromator and a polychromator options. The monochromator features a 3600 grooves/mm grating with a 0.64 m focal length, configured in a Czerny-Turner mount. The polychromator employs a 2400 lines/mm grating with a 1-meter focal length in a Paschen-Runge mount, equipped with a 20 µm motor-driven entrance slit, 35-50 µm exit slits, and 47 analytical channels.

2.3 Wavelength Selection

The selection of appropriate wavelengths is a crucial step in developing any analytical method that utilizes an emission spectrometer. GD-OES, being a relatively low-temperature excitation source, benefits from a reduced incidence of spectral interferences typically arising from abundant ionic emission lines. In the GD plasma, the population of neutral atoms from the sample significantly outweighs the ion population. Furthermore, the design of the GD source electrodes is reported to minimize matrix-related interferences [11]. These characteristics simplify the analyst's task of selecting sensitive and relatively interference-free wavelengths for the elements of interest when analyzing a Magnesium (Mg) matrix. Also being solid based technique, continuous sputtering results into deposition of sputtered material around the glow discharge crater and further leads to extinction of plasma due to contact between sputtered material and the copper anode. In view of this, simultaneous mode of analysis using polychromator has been employed, where the intensity of all the analytes are measured simultaneously using predefined PMT detectors configured to the polychromator option. Among the available wavelengths in the existing GD-OES instrument, the following wavelengths as given in Table 2 are chosen for the analysis of the Mg matrix in this study.

Table 2 Selected wavelengths for Elements of interest in Magnesium matrix

Element analyzed	Interference free wavelength (nm)
Al	394.408
Cu	324.759
Fe	373.492
Mn	403.455
Ni	349.301
Si	251.615
Ti	365.355

2.4 Standards used for calibration

Set of CRMs namely 63 MgE1, 63 MgE3, 63 MgP6 supplied by MBH Analytical Ltd, England and NCS HS 91712-1 to NCS HS 91712-6 supplied by China National Analysis Center for Iron and Steel, Beijing are used for calibrating the equipment with respect to elements Al, Cu, Fe, Mn, Ni, and Si. These CRMs are traceable to NIST through unbroken chain of comparisons. Internal Reference Materials (IRMs) prepared in-house have been used for calibration of Ti. Chemical composition of the standards used for method calibration is given in Table 3.

Table 3 Composition of standards used

Standard Name	Al (%)	Cu (%)	Fe (%)	Mn (%)	Ni (%)	Si (%)	Ti (%)
NCS HS91712-1	0.0052	-	0.0054	0.092	0.0041	0.015	-
NCS HS 91712-2	0.063	-	0.012	0.062	0.012	0.037	-
NCS HS91712-3	0.055	-	0.015	0.039	0.007	0.055	-
NCS HS91712-4	0.017	0.0054	0.0044	0.011	0.0007	0.0027	-
NCS HS91712-5	0.0062	-	0.0015	0.0054	-	0.0024	-
NCS HS91712-6	0.011	0.0016	0.0071	0.016	0.0004	0.019	-
MBH-61 MGP6 A	0.0449	0.0067	0.0041	0.0125	0.0025	0.044	-
MBH-63 MGE1 E	0.088	0.0503	0.0014	0.86	0.0162	0.052	-
MBH-63 MGE3 C	0.056	-	0.0005	1.62	0.0028	0.014	-
IRM-1	-	-	-	-	-	-	0.0035
IRM-2	-	-	-	-	-	-	0.0020
IRM-3	-	-	-	-	-	-	0.0025

3. Results and Discussion

3.1 Optimization of GD plasma conditions

For the developed analytical method targeting the Magnesium (Mg) matrix, several key operational parameters have been optimized to ensure reliable and accurate results. These included flush time prior to sputtering, pre-integration time, integration time (or) bulk acquisition time, Argon pressure maintained within the GD Plasma, and the RF power applied to the source. To maintain an Argon atmosphere which is essential for stable plasma generation, a flushing procedure was implemented. After each sample analysis, the sample is removed from the source cavity, inevitably leading to the introduction of ambient air. Therefore, upon introducing a new sample and sealing the cavity, the system is first evacuated to remove residual air, followed by flushing with Argon gas. This pre-analysis flushing not only establishes the required inert environment but also reduces the time needed for the plasma to stabilize. A flush time of 10 seconds was determined to be optimal and was applied across all experiments.

The pre-integration step serves to eliminate surface artifacts such as oxide layers and surface defects, as well as to stabilize the analytical signal before the main data acquisition. Similar to the cavity flushing, pre-integration also aids in removing contaminants like oils and breaking down molecular structures of residual vapors (e.g., water) within the discharge cavity, thereby improving the relative standard deviation for both method calibration and subsequent bulk analytical measurements [12,13]. Under the chosen operating conditions, the signal was observed to stabilize after a sputtering duration of 40 seconds. Consequently, a pre-integration time of 40 seconds was chosen for this method, followed by a bulk acquisition (integration) time of 15 seconds during which the analytical data was collected by the instrument data acquisition system**.** During the optimization process, it was noted that exceeding certain limits for RF power and Argon gas pressure resulted in excessive sputtering of the relatively soft Magnesium metal. This increased sputtering led to the deposition of sputtered material on the copper anode surface, which could interrupt the analysis. Frequent cleaning of the copper electrode became necessary under such conditions. Based on these observations, sputtering conditions of 70 W RF power and 800 Pa plasma gas pressure were identified as the optimal settings for this analytical method, providing a balance between signal intensity and plasma stability while minimizing excessive sputtering.

3.2 Calibration

Various strategies like direct calibration, calibration using Mg 278 nm line as Internal Standard (IS) and calibration using full light intensity of plasma as IS, have been studied for calibrating the equipment. Two Different parameters like Magnesium wavelength, full light intensity of plasma are studied for their suitability as IS. The correlation coefficients obtained using these methods of calibration are given in Table-4. Among the methods used, IS calibration method using full light intensity found to be having best linear fit. The correlation coefficient obtained using IS calibration using full light intensity found to be better than that of normal mode of calibration which is evident in Table 4. Hence IS calibration using full light intensity is chosen for the method.

Table 4 Calibration data obtained using different calibration strategies

Element	Direct mode of calibration	Calibration using Mg 278 nm line as IS	Calibration using Full light intensity as IS
	R^2	R^2	R^2
Al	0.985	0.995	0.997
Cu	0.990	0.998	0.999
Fe	0.987	0.998	0.998
Mn	0.994	0.994	0.996
Ni	0.990	0.990	0.990
Si	0.982	0.996	0.997
Ti	0.990	0.990	0.993

Few CRMs as per the concentration range of routine samples were subjected for replicate analysis in both direct and IS calibration and the mean, % RSD data obtained is tabulated in Table 5. It is observed that % RSD obtained using IS calibration is found to be better than direct mode of calibration. Hence it can be concluded that, IS calibration has shown improvement in precision of analysis as in IS calibration ratio of analyte intensity to IS intensity is correlated with concentration of analyte.

Table 5 CRM analysis data

Element	CRM	Actual	Direct mode		IS mode	
			Mean (%)	% RSD	Mean (%)	% RSD
Al	NCS HS91712-1	0.0052	0.0047	4.58	0.0052	3.20
Cu	NCS HS91712-4	0.0054	0.0059	3.67	0.0051	2.85
Fe	NCS HS91712-1	0.0054	0.0060	8.25	0.0055	3.83
Mn	NCS HS91712-5	0.0054	0.0053	5.27	0.0056	2.87
Ni	MBH MgP6	0.0025	0.0024	3.57	0.0025	1.57
Si	NCS HS91712-5	0.0024	0.0027	7.24	0.0026	4.21
Ti	IRM-3	0.0025	0.0024	8.21	0.0025	3.17

To validate this newly developed method, several routine samples have been analyzed and the results have been compared with those obtained from ICP-OES. The analytical data for a representative routine sample is presented in Table 6. The method demonstrated good precision, as evidenced by a RSD of less than 5%.

Table 6 Analytical data of routine samples

Element	ICP-OES		GD-OES	
	Mean (%)	% RSD	Mean (%)	% RSD
Al	0.0039	2.79	0.0036	3.01
Cu	< 0.0005	-	< 0.0020	-
Fe	0.0035	3.48	0.0036	3.75
Mn	0.0053	3.12	0.0054	2.53
Ni	< 0.0010	-	< 0.0010	-
Si	< 0.0020	-	< 0.0020	-
Ti	< 0.0020	-	< 0.0020	-

Conclusion

The developed Radio Frequency Glow Discharge Optical Emission Spectrometry (RF GD-OES) method with adequate accuracy & precision can employed for quantifying highly pure magnesium metal samples for quantifying Al, Cu, Fe, Mn, Ni, Si, Ti on regular basis. The

developed method has key advantages of high sample throughput and elimination of liquid analytical waste generation and there-by making it as analytical tool suitable for industrial laboratories managing high analytical load, especially for the chemical clearance of highly pure magnesium metal samples.

Conflicts of Interest:

Authors of this manuscript stating that "there are no conflicts to declare"

Author contributions:

Y Balaji Rao: Conceptualization; Methodology; Formal analysis; Data curation; Validation, Writing-original draft, Review & Revisions and editing

P V Nagendra Kumar: Supervision, conceptualization, resources, writing-review and editing

S NVMS Gupta: Helping in experiments, Review & Revisions and editing

Dinesh Srivastava: Supervision, conceptualization, resources, writing-review and editing

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