

## QUALITY CONTROL OF Al ALLOY BY ICP-MS

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### ABSTRACT

Laser ablation sample introduction system in combination with an inductive coupled plasma mass spectrometer (ICP-MS) is used for the investigation of elemental distribution of Al alloy. The samples are ablated by an ultraviolet laser beam at 266 nm with an energy of 4 mJ/shot at a repetition rate of 20 Hz. Samples are digested using HNO<sub>3</sub> in a microwave system and analyzed in a solution form by ICP-MS. The quantification of the analytical results is carried out using multielement solution. Quantitative data from the solution samples are used as a standard data for the laser ablation technique. The effect of Aluminum as a matrix is studied. High-resolution mass spectrometer is used to identify the Aluminum polyatomic ions in the ICP-ion source.

*Key Words: LA, ICP-MS, Al alloy, interference*

### INTRODUCTION

Cladding is essentially required in order to provide structural support for fuel in the heterogeneous reactors. Aluminum is a suitable cladding material<sup>(1-4)</sup> for use in the research reactors up to about 95 °C of cooling water temperature. Also, aluminum-base alloy containing nickel can be used in the pressurized-water reactors (PWR) up to about 300 °C. The clad material must have low neutron absorption cross-section to ensure a self-sustaining chain reaction inside the core reactor. Therefore the trace impurities (Table 1) are maintained as low as possible in the aluminum clad to increase the neutron economy. Aluminum has microscopic absorption cross-section  $\sigma_a$  equal to 0.215 barns (1 barns =  $10^{-24}$  cm<sup>2</sup>) for thermal neutrons. Boron (B) and Cadmium (Cd) must have the lowest concentration<sup>(1)</sup> in the clad material, because they have higher absorption cross-sections, 764 and 2520 barns, respectively, for thermal neutrons.

Table (1): Equivalent Boron Contents (EBC) Factor

Element	Neutron Absorption Cross Section ( $\sigma_n$ ) (Barns) at 2200 m/s	Atomic Weight	EBC
B	764	10.81	1
Cd	2520	112.41	0.3172
Co	37	58.93	0.0089
Li	70.6	6.94	0.1439
Cu	3.78	63.54	0.0008
Fe	2.56	55.85	0.0006
Mg	0.063	24.31	$\leq 0.0001$
Mn	13.3	54.94	0.0034
Si	0.13	28.09	$\leq 0.0001$
Ti	6.1	47.88	0.0018
V	5.08	50.94	0.0014
Zn	1.11	65.39	0.0002

$$\text{EBC} = [(\text{atomic mass boron})(\sigma_n \text{ impurities})] / [(\text{atomic mass impurities})(\sigma_n \text{ boron})]$$

The facility to collect signals for all masses can be used for a purely qualitative examination<sup>(5)</sup> of a sample (to identify the presence or absence of an analyte and to identify possible sources of interference). Semi-quantitative mass spectrometric analysis<sup>(6)</sup> is carried out by measuring the ion currents (these are proportional to the element concentration  $C_x$  of trace element x) mostly by means of an internal standard element with well-known concentration  $C_v$ .

$$C_x = C_v \frac{I_x A_v S_v}{I_v A_x S_x}$$

Where  $I_x$  and  $I_v$  are the ion currents measured from the internal standard v and trace element x;  $A_v$  and  $A_x$  are the respective isotopic abundances; and  $S_v$  and  $S_x$  are the respective relative element sensitivities. By neglecting the values for  $S_v$  and  $S_x$ , the analysis is considered as semi-quantitative one. The most widely used calibration method is that using a set of external calibration standards. For solution analysis these may have a simple acid or an aqueous matrix containing the analytes of interest. Several standard solutions are prepared which cover the range of expected concentrations. Under ideal conditions, measured data would form an exact linear function of concentration.

### EXPERIMENTAL

All measurements were performed using JEOL high resolution inductively coupled plasma mass spectrometer (JMS-PLASMAX2) which is installed at the Central Laboratory for Elemental and Isotopic Analysis, Nuclear Research Center, Atomic Energy Authority, Egypt (Fig. 1). The resolving power of the machine

PLASMAX2 double-focussing mass spectrometer is 12000, with this resolution, masses of the interference and element ions can easily be separated from each other. A 40.68 MHz high-frequency power supply and an automatic ignition system are used in the ICP ion source of the JMS-PLASMAX2 to obtain stable plasma.

Table (2): The experimental conditions used in the measurements

Laser Ablation conditions		Double focusing ICP-MS	
Laser type	Nd:YAG laser	Forward RF power	1300 W
Wavelength	266 nm	Reflected RF power	<2 W
Pulse duration	6 ns	Coolant gas flow rate	14 L/min
Spot diameter	60 $\mu\text{m}$	Auxiliary gas flow rate	0.3 L/min
Repetition frequency	20 Hz	Nebulizer gas flow rate	0.77 L/min
Power density	$10^{10}$ w/cm <sup>2</sup>	Mass resolution (m/ $\Delta$ m)	3000
Energy per pulse	4 mJ	Detector mode	analogue
		Optimization	Maximum ion intensity of 1 ppb of <sup>89</sup> Y <sup>+</sup>

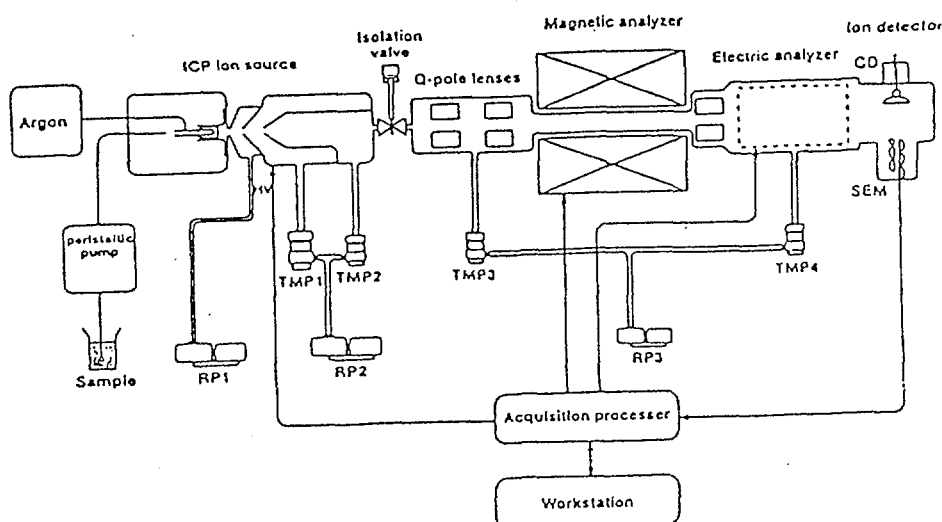


Fig. (1): Schematic overview of a JEOL PLASMAX2 high resolution ICP-MS.

## RESULTS AND DISSCUSION

In ICP-MS, large amounts of concomitant elements are known to affect analyte sensitivity and often signal suppression are observed<sup>(7-11)</sup>. For the analysis of Aluminium, the effect of Al as a matrix on the analyte sensitivity must be considered. Instrumental parameters such as the aperture sizes of the sampling and skimmer cones, the carrier gas flow, the RF power and the amount of sample reach the ICP-ion source may all have an influence on the observed matrix effect. Explanation for the matrix effect is based on two reasons. The first reason is due to the presence of the pressure of high Al [Ionization Energy = 5.99 eV and degree of ionization = 98% at 7000 °T] concentration in the plasma which contributes strongly to the electron density in the plasma and therefore shifts the ionization equilibrium ( $M \leftrightarrow M^+ + e^-$ ), so that the analyte elements are ionized to a lesser extent.

The second reason for the matrix effect is based on the space charge effect occurring after extraction of the beam from the plasma. Positive ions are mainly  $Ar^+$ ,  $O^+$ ,  $N^+$  and  $C^+$  which are present in the background. When a matrix is added the number of positive ions in the extracted beam increases. These ions repel analyte ions, and because of the increased space charge the beam is less focused by the electrostatic lenses. The analytical results of Aluminum sample by ICP-MS and LA-ICP-MS are summarized in Table (3). Calibration curves for some selected trace elements are shown in Fig. (2).

Table (3): Concentration of elements in Aluminum powder for fuel core by ICP-MS in  $\mu\text{g/g}$ .

Elements	Limits of concentration	Quantitative Analysis Meinhard Nebulizer ICP-MS	Semi-quantitative Analysis LA-ICP-MS
Boron (B)	$\leq 10$	$2.8 \pm 0.17$	$2.30 \pm 0.04$
Lithium (Li)	$\leq 40$	$20.8 \pm 0.83$	$8.78 \pm 0.99$
Cobalt (Co)	$\leq 60$	$15.03 \pm 0.90$	$8.09 \pm 0.78$
Cadmium (Cd)	$\leq 30$	$26.97 \pm 1.82$	$24.71 \pm 2.56$
Iron (Fe)	4000	$2985 \pm 179.1$	$1120.62 \pm 82.56$
Magnesium (Mg)	500	$247.8 \pm 14.87$	$268.03 \pm 13.06$
Manganese (Mn)	500	$75.55 \pm 5.29$	$316.47 \pm 31.77$
Titanium (Ti)	300	$285.82 \pm 17.14$	$169.16 \pm 17.56$
Vanadium (V)	500	$103.31 \pm 5.17$	$34.00 \pm 3.13$
Zinc (Zn)	500	$461.42 \pm 18.44$	$391.58 \pm 21.44$

More serious practical interference problems occur due to the formation of polyatomic ions. The ions as their name suggests, result from the short lived combination of two or more atomic species, e.g.  $ArO^+$ . Argon, hydrogen and oxygen are the dominate species present in the plasma and these may combine with each other

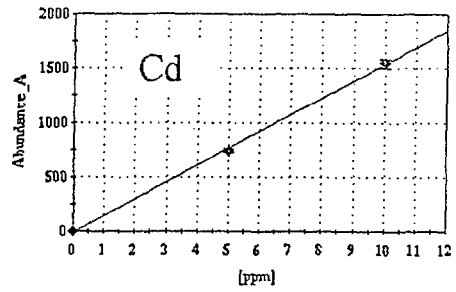
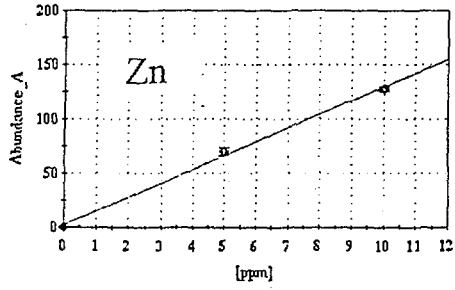
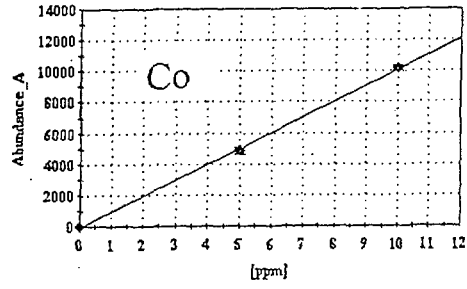
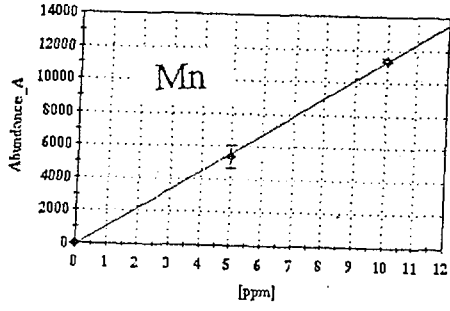
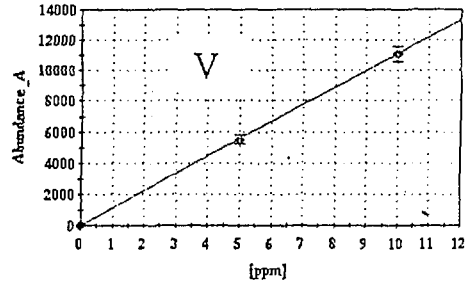
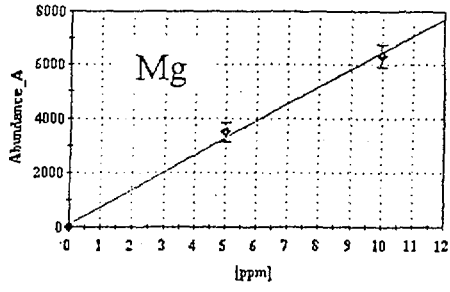


Fig. (2): Calibration curves for some selected elements.

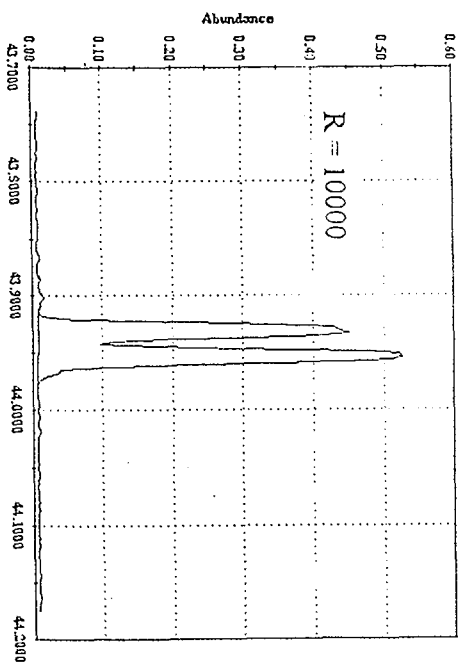
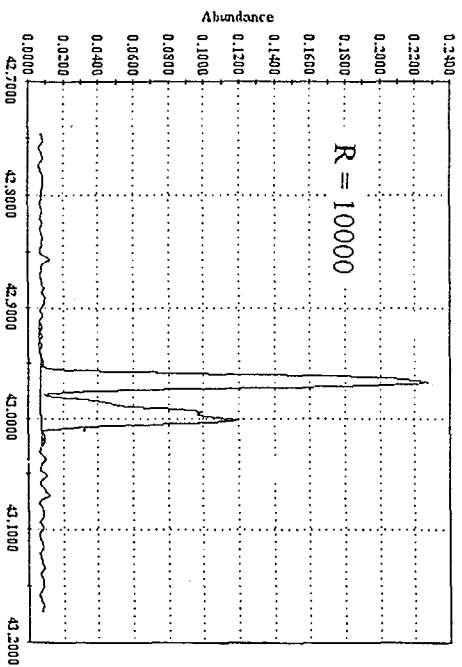
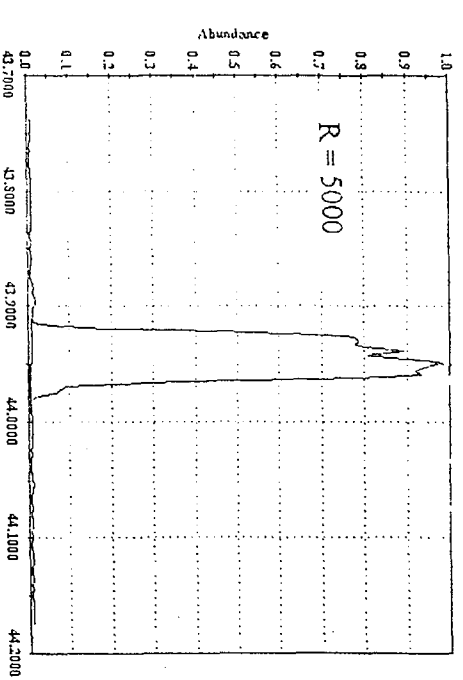
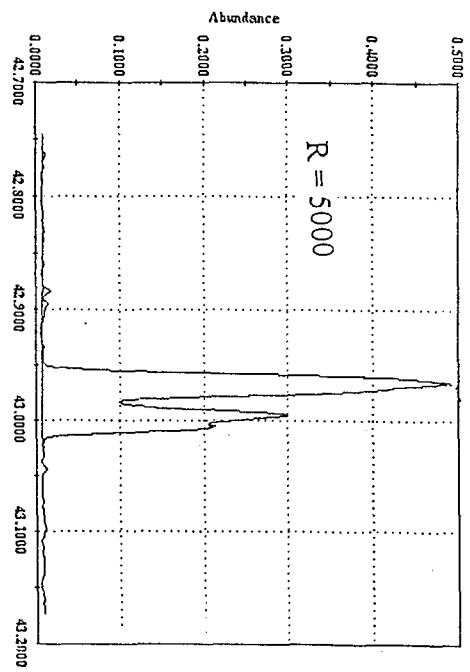
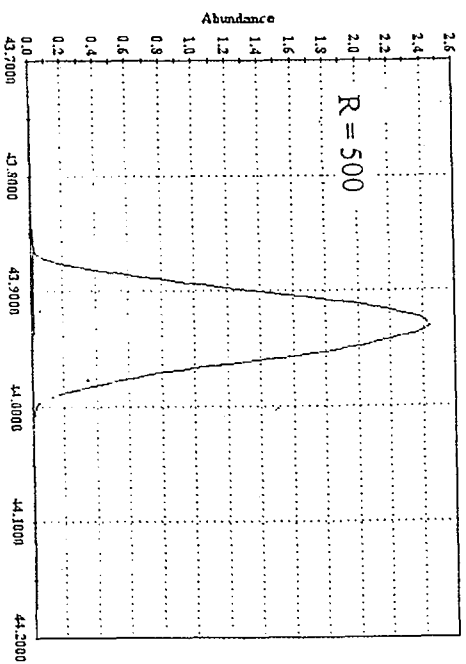
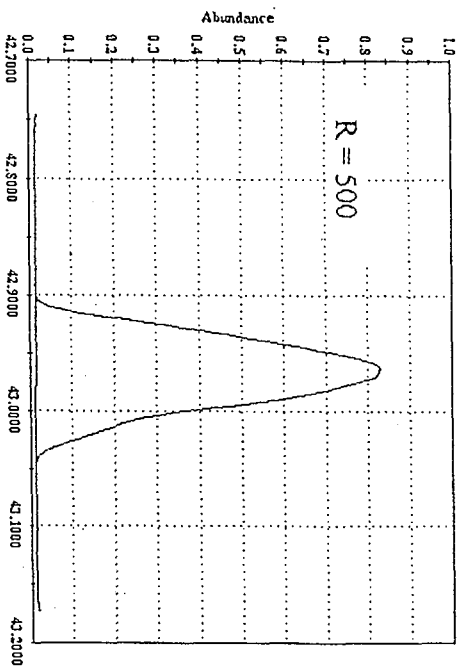


Fig. (3): Mass spectra at  $m/z = 43$ , showing the formation of  $[AlO]^+$  ion.

Fig. (4) Mass spectra at  $m/z = 44$ , showing the formation of  $[AlOH]^+$  ions.

or with elements from the analyte matrix. In some matrices refractory oxide ions are observed. These species occur either as a result of incomplete dissociation of the sample matrix or from recombination in the plasma tail. Table (4) summarizes the Polyatomic ions of Aluminum in the inductively coupled plasma mass spectrometry. Figs. (3-4) show the mass spectra at  $m/z = 43$  and  $m/z = 44$ , respectively by using the high resolution mass spectrometer PLASMAX2. By setting the resolution at different value (500, 5000, 10000),  $AlO^+$  and  $AlOH^+$  ions could be resolved from  $ArLi^+$  and  $CO_2^+$  ions, respectively.

Table (4): Polyatomic ions of Aluminum in the inductively coupled plasma mass spectrometry.

Species	Mass	Interference		Required resolution
		Species	Mass	
Al-H	27.989365	Si	27.976927	2250
		CO	27.994915	5043
		N <sub>2</sub>	28.006148	1668
Al-O	42.976455	Ar-Li	42.983548	6059
Al-O-H	43.98428	SiO	43.971842	3536
		CO <sub>2</sub>	43.98983	7925
Al-Ar	66.943924	Zn	66.927129	3986

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