Determination of trace analytes in nuclear grade Calcium Metal Samples by Axially Viewed Inductively Coupled Plasma – Atomic Emission Spectrometric technique

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Abstract

An Inductively Coupled Plasma – Atomic Emission Spectrometric (ICP-AES) method has been developed for the direct determination of 19 analytes namely, Al, B, Be, Cd, Co, Cr, Cu, Fe, Li, Mg, Mo, Mn, Ni, Pb, Pd, Si, Ta, V and W at trace concentration levels in calcium matrix. In nuclear industry, quality control and assurance of nuclear fuels and associated materials for trace metallic impurity contents form an integral part of the system for the smooth functioning of the reactor for the stipulated time span. In this context, it was required to determine trace analytes in nuclear grade Calcium which is used as a reducing agent for the production of U, Th, Pu, etc. in nuclear industry. Using axial ICP-AES, initially calibration curve for Ca with 396.847nm analytical line was obtained. Systematic studies were carried out to identify various analytical wavelengths of the analyte elements which are almost free from Ca, being the main matrix and calibration curves were obtained. For all analytes and Ca, detection limits and sensitivity values were calculated. To validate the method, three synthetic samples with analyte contents in the range of 0.1 - 5 µg/mL and Ca at 1 mg/mL were analyzed, the % recovery being in the range of 80-120% with precision better than 5% RSD. The method was found to be useful for the direct determination of the elements of interest in calcium matrix and was applied for the analysis of two nuclear grade real life calcium metal samples.

Keywords - Calcium matrix; Nuclear grade Ca metal samples; Trace metals; Axial ICP-AES

1. Introduction

High purity calcium metal has many applications in various industries. It is mainly used as deoxidizing, decarburization, desulfurization agent in alloy steel and special steel production.

It is also used as a reducing agent in high purity rare earth metal process, as an alloying agent for aluminium, beryllium, copper, lead, and magnesium alloys, and serves as a "getter" for residual gases in vacuum tubes, etc. High purity metal calcium has a wide range of applications in the pharmaceutical industry. In nuclear industry, nuclear grade calcium is used for calcio-thermic reduction for thorium, uranium, zirconium, plutonium metal preparations[1, 2]. Before being used as a nuclear grade material, high purity calcium metal needs to meet stringent chemical quality control tests including its impurity contents [3]. With this requirements, Axially viewed Inductively Coupled Plasma – Atomic Emission Spectrometric technique (ICP-AES) has been explored for the determination of trace analytes in calcium matrix during the present studies.

It is well known that ICP-AES being multielement technique has many advantages, namely, high sensitivity, reproducibility, accuracy, large linear dynamic range, less time consuming, lower limits of detection, but suffers from spectral interferences[4-10]. As ICP-AES is rich in emission spectra, there are more choices to select analytical lines relatively free from interferences for particular studies. Due to its manyfold benefits, the ICP-AES technique is used in diversified fields including nuclear industry. In literature, some authors have reported the application of ICP-AES for the determination of trace metals in calcium matrix directly and after chemical separation of the matrix [11-13].

To determine the analytes directly in presence of matrix by ICP-AES accurately, the spectral interferences from the major matrix on analytes leads to inaccurate determinations, mainly due to reduced sensitivity for usual analytical lines. To overcome this, an appropriate corrections due to any spectral interferences during the course of the analysis becomes mandatory.

During the present studies, the commercial Jobin-Yvon Axial ICP-AES (Panorama model) instrument was used. An axially viewed or end-on viewed ICP is the one wherein the observation of the plasma from its apex along the plasma column in the direction of the plasma ball takes place leading to maximum S/N and hence with better detection limits. Using this instrument various studies were carried out from our laboratory earlier and have been reported [14-15]. Also using CCD based ICP-AES unit we have reported the determination of trace metals in stainless steel, U, Th, Zr, etc. matrices[16-23]. Earlier we had carried out some studies for the determination of trace metals in calcium matrix [24]. Additional studies which were carried out further, are described here.

2. Experimental

2.1 Instrument

A Jobin-Yvon, France (Model-Panorama) axial-view ICP spectrometer, equipped with a polychromator having 35 fixed analytical channels and limited sequential facility to select any analytical line within $\pm$ 2.2 nm of the polychromator lines, was used. For nebulization, a pneumatic cross-flow nebulizer together with a peristaltic pump was employed with a sample flow rate of 1 mL/min. The resolution of the spectrometer being 0.028 nm. The main instrumental operating conditions are given in Table I.

2.2 Reagents and Preparation of Standards, Samples

Suprapur® HNO_3 acid (E. Merck, Darmstadt, Germany) and quartz doubly distilled water were used for preparation of the standards and sample solutions. Multi-element standard solutions at 20μg/ml and 5 μg/ml were prepared from commercially available Spec Pure® individual elemental stock solutions for analytes and Ca from 1 mg/ml (Johnson- Matthey Chemicals Ltd., London, UK) using appropriate dilution with 0.5 M HNO_3. Synthetic samples were prepared by adding varying amounts (0.1 – 5μg/ml) of analytes and fixed amount of Spec-pure calcium solution at 1 mg/ml and were made up to known volumes in 0.5M HNO_3. The actual real life calcium metal samples were dissolved in concentrated HNO_3 followed by evaporation to near dryness. The residues were made up to known amounts using 0.5 M HNO_3 to get 1 mg/ml Ca sample solution.

2.3 Procedure

2.3.1 Peak Search and Profile of Spectral Lines for various analytes

For this purpose, 20 μg/ml of individual analyte and Ca solutions under study were aspirated through the plasma under the standardized plasma operating conditions as mentioned in Table-1 followed by peak search, auto-attenuation and profile for the analyte lines. Calcium being the matrix element, 396.847nm was chosen as the best and most sensitive line. For other analytes, prominent lines and also free from spectral interferences were selected and the spectrometer was tuned for maximum S/N.

2.3.2 Calibration of all analytes

A two- point standardization was carried out using 0.5M HNO_3 and 5 μg/ mL of the corresponding elemental solution as the lower and higher standards and subsequently the calibration curves for each of the analytes were obtained.

2.3.3 Analysis of synthetic and actual samples

The present method did not involve any chemical separation of Ca matrix. Hence 1 mg/ml of Ca solution was fed through the plasma and the concentrations for each of the analyte at the specific wavelengths were measured. Subsequently, three synthetic samples and two actual samples were run through the plasma to record the intensity and concentration values for the analytes under study. These samples were analyzed against two-point standardization mentioned above.

3. Results and Discussion

ICP-AES is a sensitive multi- elemental technique, but has a drawback of spectral interferences. To effectively and accurately use this technique for the analysis of trace analytes in a complex matrix, it is necessary to select analytical lines for various elements under investigation which are free from interfering lines from matrix as well as from other elements. In order to minimise interference from matrix, one can choose appropriate chemical separation procedure to remove matrix. But during the process there is a possibility of contamination due to more handling of the sample and also from the reagents used. This process is adopted when it is inevitable, else choosing the most appropriate analytical lines, to study the inter-element interference effect and to carefully monitor the inference from matrix lines over analytical lines is the best option adopted so that many elements can be analysed simultaneously and accurately in less time

The present study describes an axially viewed ICP-AES based analytical method for the determination of trace analytes in high purity calcium matrix without any chemical separation. Using spec-pure Ca solution at the concentration of 1 mg/L, the most sensitive and easily accessible analytical lines for various elements were selected. If the contribution from the Ca solution on the analytical wavelength of a particular element is found to be less than the limits of detection for that element, then that particular wavelength is considered to be interference-free from calcium at that particular concentration and was used subsequently.

In Table-2, intensity values for Ca-396.847nm have been presented. Based on these values, the calibration curve for Ca was obtained and is shown in Fig.1. Detection limits for Ca was calculated as (x+3σ), where `x' is the concentration equivalent to the average of intensity of blank solution at the specific wavelength and `σ ' is the standard deviation of the blank measurements. The sensitivity was calculated based on the emission counts per concentration which is the slope of the calibration curve. The detection limits and sensitivity values for Ca as shown in the table were 0.04 μg/mg/mL and 225 counts/μg/mL respectively.

Also calibration graphs for all the 19 analytes were obtained. In Table – 3, the wavelengths used for 19 analytes (Al, B, Be, Cd, Co, Cr, Cu, Fe, Li, Mg, Mo, Mn, Ni, Pb, Pd, Si, Ta, V and W) along with detection limits(μg/mg/mL) and sensitivity (counts/μg/mL) values have been presented. In Table -4, the calibration data for analytes and Calcium (Matrix) have been shown.

To validate the method, three synthetic samples containing analytes at 0.1 μg/mL, 1 μg/mL, 5 μg/mL concentration levels in presence of 1 mg/mL of spec-pure Ca solution were analysed using optimised experimental parameters and the results for the analytes are shown in Table – 5. The results show a very good agreement between the added amounts of analytes without Ca and in presence of 1 mg/mL of Ca solution.

Hence, the developed ICP-AES method was applied for the determination of trace metals in two real life nuclear grade calcium metal samples. For all the analytes, the most sensitive lines were used. The analysis results for 19 trace elements namely, Al, B, Be, Cd, Co, Cr, Cu, Fe, Li, Mg, Mo, Mn, Ni, Pb, Pd, Si, Ta, V and W are shown in Table - 6. For Fe and Ni the values were 0.044 μg/mL and 0.015 μg/mL while for others it was below the detection limits. Thus the method was found to be satisfactory with a precision better than 5% RSD.

Conclusions

During the present studies a methodology was developed for the direct determination of trace metals in calcium matrix using axial ICP-AES without chemical separation. Though Ca matrix is less rich in emission spectra, using 1mg/ml Ca solution, spectral interference studies were carried out to identify interference free analytical lines for all the 19 the analytes, namely, Al, B, Be, Cd, Co, Cr, Cu, Fe, Li, Mg, Mo, Mn, Ni, Pb, Pd, , Si, Ta, V and W.

Based on the spectral interference study, a rapid, simple and suitable ICP-AES methodology was developed for the direct determination of trace metallic constituents in calcium matrix

without involving any chemical separation avoiding any chances of process contamination in the range of 0.05-20 µg/ml. The method was validated using three synthetic samples containing analytes at 0.1 µg/ml, 1 µg/ml and 5 µg/ml and the recovery results for the analytes were found to be satisfactory being in the range of 80 % to 120 % with precision better than 5% RSD. Subsequently two actual Ca samples were analysed for trace metal contents successfully taking into account the detection limits and the required corrections due to major Ca matrix.

Acknowledgement

Figures:
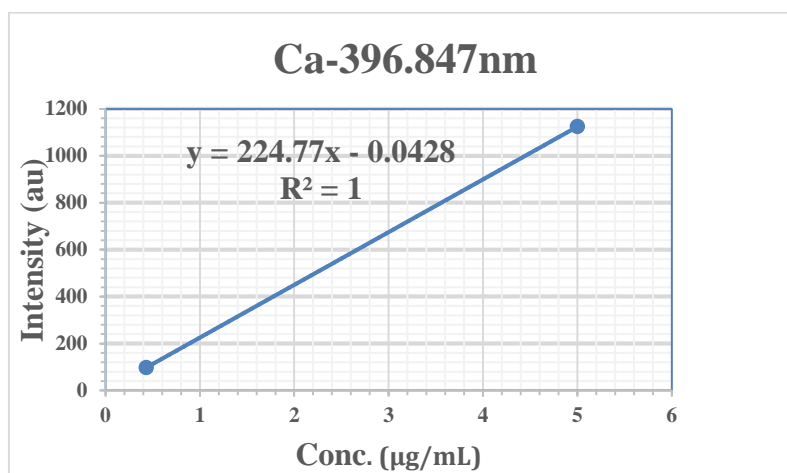
Fig. 1 Calibration Curve for Ca – 396.847nm

Tables:

Table 1 Jobin-Yvon ICP Spectrometer specifications and Operational Parameters

Model No.	Jobin-Yvon (Panorama)
Focal length	1 meter
Mounting	Paschen Runge mount
Spectral range	1650 Å – 4250 Å (With nitrogen purging)
Grating Type Rulings (grooves/mm)	Concave, holographic 3600
Spectral resolution	0.28 Å theoretical or 0.028nm
Slit width (μm)	20
Slit height (mm)	4
R.F. generator Frequency (MHz)	40.68
Power Forward power (KW) Reflected power (W)	1.0 < 20
Plasma configuration Viewing position	Horizontal Axial
Argon gas flow rates Coolant gas flow (l/min) Plasma gas flow (l/min) Nebulizer gas flow (l/min) Sheath gas flow (l/min)	16 12 1.0 0.2
Signal integration time (s)	10

Table 2 Determination of Ca by ICP-AES using wavelength 396.847nm

Ca (mg/L)	Intensity (a.u.)
Blank (0.5M HNO_3)	97
5	1124
D.L (μg/mg)	0.0395
Sensitivity (Counts/μg)	225

Table 3 Determination of Detection Limits and Sensitivity for various analytes at Specific Wavelengths

Element	Wavelength (nm)	Sensitivity (Counts/μg/mL)	Detection Limit (μg/mg/mL)
Al	308.215	43	0.0529
B	249.678	112	0.061
Be	234.861	188	0.0192
Cd	228.802	37	0.0788
Co	237.862	35	0.1141
Cr	205.559	11	0.1092
Cu	324.754	1339	0.0108
Fe	259.940	248	0.194
Li	670.776	118	0.0203
Mg	285.213	77	0.0801
Mo	281.615	20	0.1589
Mn	257.610	937	0.0138
Ni	232.003	33	0.0721
Pb	220.353	2	3.0642
Pd	340.458	32	0.0525
Si	288.158	17	0.1305
Ta	268.511	38	0.287
V	310.23	305	0.0056
W	207.911	0.85	6

Table 4 Calibration data for analytes and Calcium Matrix

Element	Wavelength (nm)	Equation of the graph
Al	308.215	Y=43.11x+0.021
B	249.676	Y=112.24x-0.0448
Be	234.661	Y=187.56x+0.0697
Cd	226.802	Y=36.947x-0.0157
Co	237.662	Y=35.086x-0.0099
Cr	205.559	Y=10.889x+0.0031
Cu	324.754	Y=1338.8x-1310.9
Fe	259.940	Y=247.42x-159.88
Li	670.776	Y=118.36x-114.55
Mg	265.213	Y=77.199x+0.0347
Mo	281.615	Y=19.772x-0.0048
Mn	257.610	Y=936.6x-932.03
Ni	232.003	Y=33.28x-31.81
Pb	220.353	Y=1.9962x-0.0005
Pd	340.458	Y=31.619x-0.0138
Si	288.158	Y=17.239x-0.0103
Ta	266.511	Y=37.584x-33.014

V	310.230	Y=305.24x+0.0127
W	207.911	Y=0.8499-0.0007
Ca (Matrix)	396.847	Y=224.77x-0.0428

Table 5 ICAP-AES Results for Synthetic samples

Element	Wavelength (nm)	Sample A 0.1 µg/ml	% Recovery	Sample B 1.0 µg/ml	% Recovery	Sample C 5.0 µg/ml	% Recovery
Al	308.215	0.11	110	0.87	87	5.50	110
B	249.676	0.09	90	1.04	104	4.3	86
Be	234.661	0.11	110	0.94	94	4.95	99
Cd	226.802	0.11	110	1.15	115	5.10	102
Co	237.662	0.12	120	1.06	106	5.6	112
Cr	205.559	0.10	100	0.95	95	5.2	104
Cu	324.754	0.12	120	1.12	120	6.10	122
Fe	259.940	0.11	110	1.11	111	6.0	120
Li	670.776	0.12	120	1.21	121	4.80	96
Mg	265.213	0.12	120	1.18	118	5.80	116
Mo	281.615	0.10	100	0.82	82	4.4	88
Mn	257.610	0.10	100	0.94	94	5.1	102
Ni	232.003	0.11	110	1.20	120	5.9	118
Pb	220.353	0.08	80	1.10	110	4.8	96
Pd	340.458	0.11	110	0.90	90	4.0	80
Si	288.158	0.08	80	0.98	98	3.90	78
Ta	266.511	0.09	90	0.92	92	4.65	93
V	310.230	0.09	90	0.84	84	4.0	80
W	207.911	0.08	80	0.9	90	4.10	82

(Values are expressed in µg/ml/mg of Ca)

Table 6 Typical ICP-AES results for real samples

Element	Wavelength (nm)	Sample 1 µg/mL	Sample 2 µg/mL
Al	308.215	BDL	BDL
B	249.676	BDL	BDL
Be	234.661	BDL	BDL
Cd	226.802	BDL	BDL
Co	237.662	BDL	BDL
Cr	205.559	BDL	BDL
Cu	324.754	0.044	0.043
Fe	259.940	BDL	BDL
Li	670.776	BDL	BDL
Mg	265.213	BDL	BDL
Mo	281.615	BDL	BDL

Mn	257.610	0.015	0.015
Ni	232.003	BDL	BDL
Pb	220.353	BDL	BDL
Pd	340.458	BDL	BDL
Si	288.158	BDL	BDL
Ta	266.511	BDL	BDL
V	310.230	BDL	BDL
W	207.911	BDL	BDL

BDL − Below Detection Limit as per Table 3
(Values are expressed in μg/ml/mg of Ca)

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