ICP-AES Determination of Trace Metallic Elements in Plutonium Samples Containing Sizeable Amounts of Americium

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ABSTRACT

During trace metallic assay of plutonium (Pu)-based fuel samples by inductively coupled plasma atomic emission spectrometry (ICP-AES), the regular procedure involves chemical separation of the major Pu matrix by solvent extraction using 30% Tri-n-butyl phosphate, TBP/CCl₄/4M HNO₃, followed by the determination of trace metals in the raffinate by ICP-AES. During this process, americium (Am) follows the chemistry of trace metals and is present in the raffinate along with the analytes of interest. Since Am is a multi-electron system rich in emission spectra, its inevitable presence in the sample may lead to overestimation of several trace elements due to its spectral interference.

The present investigations involved identification of analytical lines for the majority of trace elements free from Am interference using a high resolution ICP-AES spectrometer. It also involved development of an analytical method for the simultane-

ous determination of Am by ICP-AES and establishing correction factors for its spectral interference on other analytes as required. Based on these investigations, an analytical method was developed for ICP-AES for the determination of trace elements in Pu samples containing sizeable amounts of Am. The performance of the analytical method was evaluated by analyzing synthetic samples of Pu containing significant amounts of Am. These studies revealed that there is no appreciable contribution from the spectral interference of Am up to 300 µg/mL for analytical channels identified for the analytes using a high-resolution spectrometer. Using the analytical method developed in the present work, 25 trace elements in plutonium samples could be determined after separation of plutonium by 30% TBP/CCl₄/4M HNO₃ with the lower quantification limits of 0.1 µg/mL for critical elements (B, Cd, Dy, Eu, Gd, Sm, etc.) and 5 µg/mL for other common impurities with a precision of 2% RSD in the presence of Am.

tral interference. However, ²⁴¹Am is invariably present in these samples and its content depends on the burn-up of the irradiated fuel and age of the separated Pu sample. Typically, about 50 mg of ²⁴¹Am is produced from about 1 g of Pu generated from pressurized heavy water reactors (PHWR) per year. Chemical separation procedures followed for the removal of Pu for the determination of rare earths generally results in the presence of Am in the analyte stream. The presence of Am along with rare earths can lead to inaccurate overestimation of these elements due to its rich emission spectra (10,11).

Claudon et al. (12) reported different atomic emission lines for Am with their relative intensity using ICP-AES of moderate resolution (0.02 nm). Different authors (5-20) have determined rare earth elements using ICP-AES/MS (inductively coupled plasma emission spectrometry/mass spectrometry) after separation using high performance liquid chromatography (HPLC), liquid chromatography (LC), and ion exchange resins to avoid any erroneous analytical results due to mutual spectral interference of rare earth elements. Mazzucotelli et al. (13) tried to understand the spectral interference of common elements, e.g., Li, K, Na, and Ca, on rare earth elements. Daskalova et al. (14) reported the mutual interference of rare earth elements by ICP-AES. To date there is limited data available in the literature to understand the spectral interference of Am on common impurities and rare earth elements (Dy, Gd, Eu, Sm) which is of great importance in chemical quality

INTRODUCTION

Trace metal characterization of nuclear fuel materials is an integral part of quality assurance programs for nuclear fuel fabrication. Amongst various trace metals, specifications for elements such as B, Cd, and rare earths with very high neutron absorption cross sections are quite stringent. In order to achieve desired detection limits for

trace metals using emission spectrometric methods for quality assurance, it is necessary to separate the matrix from these analytes, thereby reducing the spectral interference from the major matrix (1-9).

In particular, rare earth elements are generally determined after their chemical separation from Pu-based fuels because of their stringent specification limits (1,2). In these separation procedures in the raffinate-containing analytes, major matrix elements are reduced to the level of <20 µg/mL to avoid spec-

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assurance programs related to nuclear fuel fabrication (21).

In the present work, investigations were carried out to develop analytical methods for the determination of trace metallic constituents in Pu-based samples containing Am and using ICP-AES analysis. The investigations involved identification of interference-free analytical lines for the simultaneous determination of Am and the spectral interference of Am on the analytical lines of all trace metallic constituents. In order to carry out this study, high purity Am was one of the primary requirements. In the course of these investigations, a method for obtaining high purity Am from the analytical waste was developed (15) and the purity of Am thus obtained was ascertained using ICP-AES and neutron activation analysis. Required spectrometric investigations were carried out for the development of a methodology for trace metal assay of Pu-based samples.

EXPERIMENTAL

Instrumentation

All of the atomic emission spectrometric studies were carried out using a Jobin-Yvon Ultima high resolution ICP-AES (22). It has the practical resolution of ≤ 0.005 nm and a spectral range of 200–800 nm. The specifications and operating conditions of the instrument are listed in Table I.

Reagents and Standard Solutions

Rare earth elements and other common impurity standard solutions were prepared from high purity solutions (E. Merck, Darmstadt, Germany) by suitable dilutions with 0.5M HNO₃. Suprapur® (E. Merck) HNO₃ and quartz double-distilled water were used for preparing 0.5M HNO₃. Tri-n-butyl phosphate (TBP) was procured from Koch-Light Laboratories Pty. Ltd., Johannesburg,

South Africa. The calibration plots for each analyte were obtained by using multiple standards having analyte concentrations in the 0–100 µg/mL range. High purity Am stock solutions were prepared in our laboratory from analytical waste after the three-step separation procedure was used. Analytical waste contained uranium, iron, sodium, and calcium as major constituents along with milligram amounts of americium. Separation and purification was accomplished by using a three-stage separation procedure involving solvent extraction methods using (a) U-separation by 30% Tri-n-butyl phosphate (TBP) in n-dodecane, (b) Fe and Na separation by 0.1M N,N,N',N' tetraoctyldiglycolamide (TODGA) + 0.5 M di-hexyl octanamide (DHOA) in n-dodecane and Ca separation by octyl phenyl-N,N-diisobutyl carbamoylmethyl phosphine oxide (CMPO) column chromatographic extraction (15). From the stock solution, different concentrations

of Am in the 0.05–100 µg/mL range were prepared using proper dilutions with 0.5M HNO₃. Blank correction was carried out using 0.5M HNO₃.

RESULTS AND DISCUSSION

The element ²⁴¹Am, which is invariably present in Pu-based fuel samples due to the β decay of ²⁴¹Pu, follows the chemistry of analytes like rare earth elements during the separation of the Pu matrix by solvent extraction using TBP as an extractant. Consequently, the presence of appreciable amounts of Am in raffinate along with other analytes can lead to spectral interference during trace metallic impurity analysis of Pu-based samples by ICP-AES due to its line-rich emission spectra (10,11). Since it is cumbersome to prepare high purity spectroscopy-grade Am (23), there is very little literature available on the spectral interference of Am on concomitant analytes having stringent

TABLE I
HR-ICP-AES Specifications and Operating Conditions

Spectrometer		Model	ULTIMA HR-ICP-AES
Optical design		1m Czerny Turner	
Grating	Holographic, ion-etched optical grating – two		
Groove density	2400 grooves/mm, 4320 grooves/mm		
Grating size	110X110 mm		
Wavelength range	120-800 nm		
Band pass	0.0023 nm from 120–340 nm 0.0046 nm from 340–800 nm		
Thermal regulation	Controlled to 30 ± 1 °C		
RF Generator			
Frequency		40.68 MHz	
Oscillator		27.12 MHz	
Pump		Dual channel (12 roller)	
Nebulizer		Pneumatic and concentric	
Operating Conditions			
Ar plasma flow		13 L/min	
Integration time		10 s	
Reflected power		< 10 W	
Sample rate		1 mL/min	

specification limits for Pu-based fuel samples. In our laboratory, high purity Am was obtained after using the three-step separation procedure (15) to study the spectral interference of Am on the trace metals and to arrive at correction factors due to the spectral interference of Am on the line measurements of the analytes. However, since the correction factor depends on the concentration of interfering elements, interference-free analytical lines, if possible, were required to be chosen for the accurate and precise determination of Am. The following steps were undertaken in the present study: (a) Determination of Am by ICP-AES; (b) spectral interference of Am on the regularly used analytical lines of concomitant analytes, and (c) validation of the methodology.

Determination of Am by ICP-AES

Claudon et al. (12) reported some of the Am emission lines with their relative intensities and spectral interference in the presence of U and Pu. In the present studies, two of these Am lines, i.e., at 283.236 nm, the most intense line of Am (see Figure 1), and 408.930

nm, were investigated for their linear estimation range and the spectral interference from concomitant analyte elements in the raffinate obtained after chemical separation of Pu using the solvent extraction procedure with 30% TBP/CCl₄/4M HNO₃. Table II lists the calibration data for the Am analytical lines. Figures 2 and 3, respectively, show the linear calibration curves for these analytical lines obtained for Am using Am solutions with concentrations ranging from 0.5 to 100 µg/mL. It was found that in both cases Am could be determined simultaneously by ICP-AES up to 100 µg/mL of Am with an RSD of ~2%. In order to validate the analytical method, synthetic samples were analyzed by using ICP-AES and radiometric methods. The results obtained by ICP-AES were in good agreement with the radiometric determinations (Table III). Spectral interference from concomitant analytes on the identified lines of Am were studied using 1000 µg/mL concentrations of the corresponding elements. It was observed that for the Am analytical lines at 283.236 nm and 408.930 nm, the contributions from Cr, Dy, Eu, Fe, Gd, and Sm were negligibly small (Table IV) and both

lines can be used for the ICP-AES determination of Am (Table V).

Spectral Interference of Am on Regularly Used Analytical Lines of Concomitant Analytes

To develop the methodology for trace metallic impurity analysis by ICP-AES for Pu-bearing samples containing Am, the most important step is to study the spectral interference of Am on the analytes having stringent specification limits for Pu-based fuels. Using 100 µg/mL of high purity Am solution, spectral interference studies were carried out. For distinguishing the apparent concentration due to the spectral interference from the impurity content in purified Am, more than one analytical line was chosen for each analyte for their determination. The variation in estimated value in purified Am for the given element with the use of its different analytical channels was construed to be due to spectral interference, while nearly constant estimation using different analytical channels was interpreted as being due to its presence in purified Am as an impurity. The analytical line providing lowest concentration is least interfered

Fig. 1. Emission profile of Am (283.236 nm) line.

TABLE II
Calibration Data for Am Analytical Lines

Americium lines (nm)	283.236	408.930
Slope (counts µg/mL)	10899.59	3660.31
Regression coefficient (R)	0.9999	0.9997

TABLE III
ICP-AES Determination of Am

Conc. of Am by Radiometry (µg/mL)	Using 283.236 nm line of Am (µg/mL)	Using 408.930 nm line of Am (µg/mL)
0.5	0.5 ± 0.04	0.43 ± 0.04
5.0	5.4 ± 0.5	5.3 ± 0.5
10.0	10.3 ± 1	10.6 ± 1
20.0	20.8 ± 2	21 ± 2
100	108 ± 5	106 ± 5

Fig. 2. Calibration curve for Am 283.236 nm line.

Fig. 3. Calibration curve for Am 408.930 nm line.

TABLE IV
Interference of Other Analytes
on Am 283.236 nm Line

Element	Am Analytical Line (nm)	Concentration Tested (μg/mL)	Contribution on Am Line (μg/mL)	Correction Factor
Cr	283.236	1000	< 0.05	-
Dy		1000	< 0.05	-
Eu		1000	< 0.05	-
Fe		1000	< 0.05	-
Gd		1000	0.265	2.65×10^{-4}
Sm		1000	< 0.05	-

TABLE V
Interference of Other Analytes
on Am 408.930 nm Line

Element	Am Analytical Line (nm)	Concentration Tested (μg/mL)	Contribution on Am Line (μg/mL)	Correction Factor
Dy	408.930	1000	1.68	1.68×10^{-3}
Eu		1000	0.18	1.8×10^{-4}
Gd		1000	3.51	3.51×10^{-3}
Sm		1000	0.173	1.73×10^{-4}

and, in general, the analytical lines showing the presence of elements below the limits of quantification were chosen as interference-free. Table VI shows that for the elements Ag, Al, Ca, Co, Cr, Dy, Eu, Fe, Mn, Na, Ni, Pb, and Sm, there was no contribution of up to 100 μg/mL of Am on their respective analytical lines. The results of the determination of trace elements in the purified Am (at 100 μg/mL) using more than one analytical channel of the corresponding elements are listed in Table VII. Gd has analytical lines at 310.050 nm, 335.048 nm, 342.247 nm, and 379.639 nm. Estimation of Gd in high purity Am solution using these analytical lines was found to be within the $\pm 5\%$ range. This fact indicated the presence of Gd as an impurity in the high purity Am matrix since all spectral lines of Gd cannot be affected to the same extent. The same conclusions can be drawn for the values obtained in case of Mg at the 279.553 nm and 285.213 nm lines and Cu at the 213.598 nm, 224.700 nm, and 324.754 nm lines. Nevertheless, for Cu at the 283.26 nm line, there was a large increase in background. This was probably due to the wings of the most intense line

TABLE VI
Spectral Interference of Am
on Other Analytes

Element	λ (nm)	100 $\mu\text{g/mL}$ of Am
Ag	328.068	BDL
Al	309.271	BDL
Ca	393.366	BDL
Cd	228.802	BDL
Co	238.892	BDL
Cr	283.563	BDL
Dy	353.170	BDL
Eu	420.505	BDL
Fe	259.940	BDL
Mn	257.610	BDL
Na	588.995	BDL
Ni	221.647	BDL
Pb	220.353	BDL
Sm	359.262	BDL
U	385.958	BDL

BDL (background detection limit) = $<0.05 \mu\text{g/mL}$

of Am (283.236 nm). It can be inferred that in the presence of Am, Cu at the 283.260 nm line was highly interfered and should be avoided as an analytical line for Cu estimation.

Validation of Methodology

The determination of trace elements in nuclear materials (4-5,7-9) is an important feature of analytical chemistry in the nuclear field. For this purpose, ICP-AES-based techniques have been employed which requires chemical separation of Pu. The analytical lines identified as free from spectral interference of Am were used subsequently for the ICP-AES determination of trace metals in Pu-based samples. Pu was separated using the well-known 30% TBP/ CCl_4 /4M HNO_3 extraction procedure (24). To validate the methodology, synthetic samples

TABLE VII
Trace Elements Present in Purified Am

Element	λ (nm)	Concentration ($\mu\text{g/mL}$)	Concentration ($\mu\text{g/mL}$)
Gd	310.050	0.98	1.03 ± 0.05
	335.048	1.01	
	342.247	1.12	
	379.639	1.02	
Mg	279.553	0.40	0.38 ± 0.02
	285.213	0.36	
Zn	206.191	0.34	0.38 ± 0.06
	334.502	0.36	
	213.856	0.44	
Cu	324.754	0.11	0.10 ± 0.01
	213.598	0.10	
	224.700	0.10	
	283.260	396	

This value is not included in the average for Cu. ^a

^a The value obtained by monitoring 283.260 nm Cu emission line is very high in contrast to those obtained using Cu emission 324.754, 213.598, and 224.700 nm. This suggests that Am with its emission at 283.236 nm spectrally interfered at this wavelength for Cu.

were prepared using high purity PuO_2 (power reactor grade Pu). A 5-g amount of PuO_2 powder was dissolved in HF-HNO_3 mixture and the feed was adjusted to 3.5M HNO_3 . Five synthetic samples were prepared: Am blank (containing Am at 280 $\mu\text{g/mL}$), Am blank spiked with 0.1 $\mu\text{g/mL}$, 1 $\mu\text{g/mL}$ of critical elements (e.g., B, Cd, Eu, Sm, Gd, Dy, Ag, etc., having lower specification limits for Pu-based fuel samples), and Am blank spiked with 0.5 $\mu\text{g/mL}$, 5 $\mu\text{g/mL}$ of 18 common impurities. Seven contacts of 30% TBP/ CCl_4 with aqueous:organic (1:1) were used for the removal of Pu from each synthetic sample. Quantitative removal of Pu was confirmed by radiometric analysis. All of these synthetic samples were analyzed for trace metals by ICP-AES in addition to Am where both the analytical channels mentioned

earlier of Am were used. The analytical results for the above-mentioned analytes with their specified analytical channels are given in Tables VIII and IX. From these data it was observed that the % recovery was within the acceptable limits for these elements.

This fact suggested that critical elements can be determined in the presence of $\sim 300 \mu\text{g/mL}$ Am at the 0.1 $\mu\text{g/mL}$ level (Table VIII), whereas for common impurities, the level can be as low as 5 $\mu\text{g/mL}$ (Table IX). The methodology developed in the present study can be used effectively for the ICP-AES determination of trace elements in Pu-based fuel samples containing sizeable amounts of Am.

TABLE VIII
Determination of Critical Elements in Synthetic Samples of Pu Containing Sizeable Amounts of Am

Element	Analytical Line	Sample-1				Sample-2			
		Am Blank (µg/mL)	Amount Added (µg/mL)	Amount Estimated (µg/mL)	% Recovery	Am Blank (µg/mL)	Amount Added (µg/mL)	Amount Estimated (µg/mL)	% Recovery
Am	283.236	280 ± 10	-	290± 10	-	280 ± 10	-	290± 10	-
Am	408.930	280 ± 10	-	290± 10	-	280 ± 10	-	290± 10	-
Ag	328.068	<0.05	0.1	0.09	90	<0.05	1	0.7	70
B	249.773	0.18	0.1	0.30	120	0.18	1	0.28	100
Be	313.042	<0.05	0.1	0.1	100	<0.05	1	1	100
Cd	228.802	<0.05	0.1	0.09	90	<0.05	1	0.9	90
Dy	353.170	<0.05	0.1	0.1	100	<0.05	1	0.9	90
Eu	420.505	<0.05	0.1	0.08	80	<0.05	1	0.8	80
Gd	342.247	<0.05	0.1	0.08	80	<0.05	1	0.9	90
Sm	359.262	<0.05	0.1	0.07	70	<0.05	1	0.8	80

TABLE X
Determination of Common Elements in Synthetic Samples of Pu Containing Sizeable Amounts of Am

Element	Analytical Line	Sample-3				Sample-4			
		Am Blank (µg/mL)	Amount Added (µg/mL)	Amount Estimated (µg/mL)	% Recovery	Am Blank (µg/mL)	Amount Added (µg/mL)	Amount Estimated (µg/mL)	% Recovery
Am	283.236	280 ± 10	-	290± 10	-	280 ± 10	-	290± 10	-
Am	408.930	280 ± 10	-	290± 10	-	280 ± 10	-	290± 10	-
Al	309.271	1.7	0.5	2.1	80	1.9	5	6.9	100
Ca	393.366	4	0.5	4.5	100	4	5	9.3	103
Co	238.892	<0.05	0.5	0.5	100	<0.05	5	5.0	100
Cr	283.563	0.3	0.5	0.75	90	0.3	5	5.4	102
Cu	224.700	0.1	0.5	0.6	100	0.1	5	5	98
Fe	259.940	2.2	0.5	2.7	100	2.2	5	7.4	104
Ga	250.017	0.4	0.5	0.9	100	0.4	5	5.6	104
In	303.936	0.2	0.5	0.7	100	0.2	5	5.2	100
Mg	279.553	0.8	0.5	1.3	100	0.8	5	5.9	102
Mn	257.610	0.1	0.5	0.6	100	0.1	5	5.3	104
Mo	202.030	0.3	0.5	0.8	100	0.3	5	5.5	104
Na	588.995	3.2	0.5	3.75	110	3.2	5	8.2	100
Ni	221.647	0.2	0.5	0.7	100	0.2	5	5.2	100
Pb	220.353	0.5	0.5	0.9	80	0.5	5	5.8	106
V	309.311	<0.05	0.5	0.5	100	<0.05	5	5.1	102
W	207.911	1.1	0.5	1.6	100	1.1	5	6.3	104
Zn	213.856	2.9	0.5	3.35	90	2.9	5	8.0	102

CONCLUSION

Plutonium (Pu) plays a key role in the development of atomic energy programs based on the closed-end nuclear fuel cycle. This involves reprocessing of the irradiated fuel and the use of reprocessed Pu in the fabrication of second-generation reactors as mixed oxide fuel. For quality control and quality assurance of nuclear fuels for second-generation reactors, it is necessary to determine the trace metal content in the nuclear fuel material. The americium (Am) concentration associated with Pu depends on its burn-up and storage.

In the present work, a suitable methodology was developed for the determination of trace metallics in Pu-based fuel samples containing sizeable (up to 300 µg/mL) amounts of Am. The analytical method involved chemical separation of Pu and analysis of the raffinate for trace metal determination by inductively coupled plasma atomic emission spectrometry (ICP-AES). Since Am associated with Pu is present in the raffinate, the investigations were carried out in order to understand the spectral interference from Am and to analyze the raffinate for Am by ICP-AES in the presence of concomitant trace elements.

These studies resulted in identifying the analytical lines for 25 trace metals free from spectral interference of Am using a spectrometer having a practical resolution of 0.005 nm. For the estimation of Am, the analytical lines that are free from spectral interference of concomitant analytes were also identified. Using the ICP-AES technique, 25 trace elements along with Am were determined with a precision of 2% RSD. The method was validated by analyzing synthetic samples in the presence of ~300 µg/mL of Am with a low detection limit in the range of 0.1 µg/mL for critical elements (B, Cd, Dy, Eu, Gd, Sm,

etc.) and 5 µg/mL for other common impurities.

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