Inter-element Effects in the Determination of Trace Amounts of Plutonium by High Resolution Inductively Coupled Plasma Atomic Emission Spectrometry

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INTRODUCTION

Plutonium (Pu) is a highly toxic, fissionable element that is used for power generation in nuclear reactors. Since plutonium is produced in large amounts during the operation of nuclear power plants, it is essential for public health and nuclear safeguards to develop sensitive, accurate, and rapid analytical methods for the determination of Pu in the nuclear fuel cycle program. The recovery of Pu and uranium (U) from all types of scraps and residues, as well as the removal of Pu and other trans-uranic elements from radioactive wastes, are highly pressing problems from an economical and ecological point of view. Determination of Pu at trace levels is of utmost importance in the assay of waste solutions generated in radiochemical laboratories. It is also imperative to monitor the trace quantities of Pu left in the raffinate after extraction of Pu by suitable chemical separation procedures. The presence of significant amounts of Pu in view of its complex spectra can cause spectral interferences resulting in the over-estimation of the analytes of interest. Thus, determination of Pu at trace levels in aqueous solutions is an important aspect of the nuclear fuel cycle. The methods of α -counting, γ -spectrometry, inductively coupled plasma atomic emission spectrometry (ICP-AES), and isotope dilution mass spectrometry (ID-MS) have been used in the

ABSTRACT

An analytical method was developed for the determination of plutonium (Pu) in aqueous solutions using high resolution inductively coupled plasma atomic emission spectrometry (ICP-AES). The analytical range for Pu in aqueous solution was 0.1 to 100 $\mu\text{g/mL}$. The validity of the method was established by analysis of several synthetic samples of plutonium. Plutonium was estimated in synthetic samples in the presence of uranium, thorium, rare earths, and common metallic elements after applying inter-elemental correction factors for the interfering elements. Radiometric methods were employed for an independent cross-check of the values obtained by ICP-AES.

The results obtained by ICP-AES and the radiometric method were in good agreement with a precision of 10 to 20% at very low concentrations of Pu and better than 5% at higher concentration levels.

The method is useful for the determination of Pu in different types of aqueous waste solutions generated in radiochemical laboratories, and also to monitor the trace levels of Pu left in the raffinate after its chemical separation along with other metallic constituents. It should be noted that the presence of large amounts of Pu in the raffinate can lead to an over-estimate in measured concentrations of the analytes of interest due to its rich emission spectrum.

nuclear industry for monitoring the Pu content. The relative sensitivities (1) of these techniques are listed in Table I. Fast and reliable methods for the determination of plutonium (Pu), uranium (U), and thorium (Th) in samples are ICP-AES and α -counting. However, when samples contain large concentrations of elements having rich emission spectra (such as uranium, rare earths, thorium, etc.), chemical separation of these interfering elements would be required prior to ICP-AES analysis. ICP-AES has been successfully employed for the determination of common metallic elements and rare earths in a variety of nuclear fuels of interest (2-7). To our knowledge, only a few reports (8-12) have been published using ICP-AES for the determination of Pu. The simultaneous determination of americium (Am) and plutonium by ICP-AES has been reported by Claudon et. al. (11). A comparison of instrumental methods used in the determination of U and Pu has been reported by Carmen Sabau et. al. (13).

The aqueous solution generated in a reprocessing plant contains traces of plutonium, uranium, fission products, and other common metallic elements such as Fe, Ni, Cr, Mn, etc. In addition, Advanced Heavy Water Reactor (AHWR) fuels that will be used in the future are based on the combination of Th with other co-contaminants such as (Th-Pu) and (Th-U). This necessitates the development of a method to determine Pu in the presence of other co-contaminants.

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In this paper, an analytical method has been developed for the determination of Pu in an aqueous medium as well as in the presence of uranium, thorium, rare earths, and certain common metallic constituents using high resolution ICP-AES spectrometry.

EXPERIMENTAL

Instrumentation

The instruments used in the present studies was a Jobin Yvon Ultima ICP-AES (Longjumeau Cedex, France), equipped with an R.F. generator at a frequency of

40.68 MHz. The monochromator consisted of two holographic gratings with 4320 grooves/mm and 2400 grooves/mm covering different range with back-to-back vertical fitting. The sample introduction system had a Meinhard® TR 50-C1 glass nebulizer and a cyclonic spray chamber. The instrumental operating conditions are listed in Table II.

Standard Solutions and Reagents

A 100-mg amount of pre-analyzed PuO₂ was dissolved in a mixed acid of concentrated HNO₃+0.35 M HF which was evaporated to near dryness. Then, 4M HNO₃ was added to the residual solution. This step was repeated three times to ensure removal of HF. This solution was diluted in 10 mL of 4M HNO₃ to obtain a Pu standard of 10 mg/mL concentration. The standard solution was subsequently employed to prepare a series of Pu solutions in the 0.02 to 100 µg/mL concentration range after appropriate dilution.

The reagents used in the preparation of the standards and samples were of electronic grade purity. The water used was doubly distilled in a quartz apparatus prior to its use.

Synthetic Samples

To gain confidence in the determination of plutonium, nine synthetic samples at different Pu concentrations were prepared and analyzed by the standardized procedure. Several of these synthetic samples were also analyzed by radiometric methods to ascertain the Pu concentration. Appropriate dilutions were used in the radiometric techniques to obtain the net counts within the range of the detector employed. Corrections for the ²⁴¹Am concentration were also performed by monitoring with gamma spectrometry.

TABLE I

Relative Sensitivities of Different Techniques for Pu Determination

Techniques	
α-spectrometry	1 pg
γ-spectrometry	µg/mg
Inductively coupled plasma mass spectrometry (ICP-MS)	< 1000 fg
Inductively coupled plasma atomic emission spectrometry (ICP-AES)	15 ng
ICP laser-excited atomic fluorescence spectrometry (LEAFS)	50-500 ng
Coulometry	200 pg
Titrimetry	1-100 mg

TABLE II

ICP-AES Instrumental Operating Conditions

Model	Ultima ICP-AES
Focal Length	1M
Grating	Two holographic gratings with 4320 grooves/mm and 2400 grooves/mm
Range Covered	(a) 180-450 nm; (b) 400-800 nm
R.F. Generator Frequency	40.68 MHz
Forward Power	1.0 KW
Reflected Power	< 10 W
Nebulizer	Meinhard TR 50-C1 glass
Pressure Input	3 bars
Spray Chamber	Cyclonic
Plasma Torch	Demountable torch assembly with three co-axial concentric tubes; central injector of alumina and two quartz tubes
Argon Plasma Gas Flow	12 L/min
Cooling gas flow	0.2 L/min
Nebulizer Pressure	3 bars
Nebulizer flow	0.85 L/min
Pressure of the Manometer	6 bar
Pump Speed	20 rotations /min
Sample Uptake Rate	1 mL/min

Our earlier studies show (5, 14) that Pu concentrations of <25 µg/mL do not significantly contribute to the preferred analytical wavelengths for the common elements Al, Ag, B, Ca, Cd, Co, Cr, Cu, Fe, Ga, Mg, Mn, Na, Ni, Pb, Sr, Zn, and the rare earths Ce, Dy, Eu, Gd, Sm, and Tm. Hence, most of the interference studies in the present work were carried out with 10 µg/mL Pu. To study the effect of uranium, thorium, and rare earths (known for their rich emission spectrum) on the determination of Pu, spiked samples having a 10-µg/mL Pu concentration along with varying concentrations of concomitant elements at different Pu:concomitant element concentration ratios of 1:0, 1:1, 1:5, and 1:10 were prepared. The effect of the common metallic concomitants (Al, Ag, B, Ca, Cd, Co, Cr, Cu, Fe, Ga, Mg, Mn, Na, Ni, Pb, Sr, and Zn) on Pu estimation was also investigated. This was done by spiking a 10-µg/mL Pu concentration with 10, 50, and 100 µg/mL each of an E. Merck standard (Darmstadt, Germany) for each of the above elements. The standard containing these concomitants at 1 mg/mL was appropriately

diluted with 1 M HNO₃ to obtain standards with varying concentrations of these elements. The concentration of each standard was confirmed using ICP-AES analysis.

PROCEDURE

A detailed spectral scan for the ICP plutonium lines ranging from 250-500 nm was carried out by aspirating 25 µg/mL Pu into the plasma. Feasibility studies were carried out at five Pu wavelengths (296.464, 300.057, 340.110, 363.221, and 453.615 nm) as reported in the literature (8,10). The instrumental parameters were optimized for positioning of the analytical line with appropriate sensitivity on the photomultiplier tube. The Pu lines at 300.057 nm and 453.615 nm were selected since they provided the optimum signal-to-noise ratio. With our instrument, a four point standardization containing Pu concentrations of 0.2, 10, 50, and 100 µg/mL was employed to obtain the calibration curve for the two analytical Pu lines. The calibration curves obtained for the Pu lines at 300.057 and 453.615 nm are shown in Figure 1.

Analysis of the standards was carried out to determine the precision and accuracy of Pu determination. For all Pu standards, eight replicate measurements were performed. The slope and intercept for the calibration curves along with error bars for Pu (300.057 and 453.615nm) are included as an insert in Figure 1. A series of spiked samples was analyzed to study the possible inter-element effects. The Pu content in the presence of the interferents was monitored using the two Pu analytical lines mentioned above. Inter-element correction factors were evaluated by aspirating 500 µg/mL of the individual elemental SpecPure® solutions of Co, Cr, Cu, Fe, Mn, Ni, Dy, Eu, Gd, Sm, Th, and U into the ICP-AES. Figure 2 shows typical spectral profiles at 300.057 nm of: (a) 10 µg/mL Pu + E. Merck multi-elemental standard (common impurity mixture (CIM) containing Al, Ca, Co, Cd, Cr, Cu, Fe, Mg, Mn, Na, Ni, and Pb each at 10 µg/mL; (b) 10 µg/mL Pu + 50 µg/mL of CIM; and (c) 10 µg/mL Pu + 100 µg/mL CIM; (d) 10 µg/mL Pu.

Fig. 1. Calibration curve for Pu (300.057 nm) and Pu (453.615 nm).

Fig. 2. Profiles for Pu at 300.057 nm in absence and in presence of varying common metallic impurity elements CIM : Common elements impurity mixture.

Figure 3 shows the profiles obtained at 300.057 nm for 10 µg/mL Pu and a mixture of Pu and rare earths in (a) Pu(10 µg/mL) + REE (10 µg/mL), (b) Pu(10 µg/mL) + REE (50 µg/mL), (c) Pu(10 µg/mL) + REE (100 µg/mL), (d) Pu(10 µg/mL). As can be seen from Figures 2 and 3, there is a marginal increase in the background and a significant spurious increase in the peak intensity above the 1:5 ratio for the common elements (Al, Ca, Co, Cd, Cr, Cu, Fe, Mg, Mn, Na, Ni, and Pb) and the rare earth elements (Ce, Dy, Eu, Gd, Sm, and Tm) above the 1:10 ratio. Similar features were observed for the Pu line at 453.615 nm, except that the effect is more pronounced for the rare earths above the 1:5 ratio (Pu:REE), while for common elements it was above the 1:10 ratio (Pu:CIM). Uranium and thorium also exhibit similar trends in their spectral profiles.

The analytical range obtained in aqueous solution was 0.1–100.0 µg/mL for Pu at 300.057 nm; for 453.615 nm, it was 0.2–100 µg/mL. The detection limit calculated as

the concentration corresponding to a signal equal to the blank signal plus three times its standard deviation (15) was 30 µg/L for Pu at 300.057 nm and 70 µg/L for Pu at 453.615 nm.

A comparison of the detection limits obtained for Pu by different workers is given in Table III. The limits obtained in the present studies are better than those reported by Edelson et al. (8), Kulkarni et al. (12), and Claudon et al. (11), but comparable to those reported by Manika et al. (9) and Huff and Bowers (10). Observed differences are very likely due to variations in the optical systems and the experimental excitation conditions.

Table IV lists the estimates (based on eight replicate measurements) obtained for Pu in nine synthetic samples without the presence

of any concomitant interfering elements. There is close agreement between the Pu amount expected and determined in the present studies. The variation is between 3–6% at Pu concentrations ranging from 10–100 µg/mL; though the variation was 10% at the lower concentration of 1 µg/mL.

SPECTRAL INTERFERENCE STUDIES

It is well known that transitional elements, rare earths, thorium, and uranium have complex spectra (rich emission lines) and the presence of spectral lines in the close vicinity of the chosen analytical line can cause an over-estimate of the analytes of interest. This is also reflected in the spectral profile studies of the Pu lines at 300.057 and 453.615 nm for different sets

TABLE III
Plutonium Detection Limits (µg/L)

λ (nm)	Present*	(Ref. 12) (Kulkarni) (1990)	(Ref. 8) (Edelson) (1986)	(Ref. 11) (Claudon) (1987)	(Ref. 10) (Huff) (1990)	(Ref. 9) (Mainka) (1983)
300.057	30	200	54	100	28	20
453.615	70	100	15	220	89	Not Reported

* Based on the formula: Concentration corresponding to analytical signal = $X_{bl} + 3 S_{bl}$, where X_{bl} = average signal for blank; S_{bl} = standard deviation in the determination of blank.

TABLE IV
Analytical Results for the Determination of Plutonium in Synthetic Samples

Analysis of Synthetic Samples (conc. in µg/mL)	at 300.057 nm (conc. in µg/mL)	at 453.615 nm (conc. in µg/mL)
0.2	0.21 ± 0.02	0.24 ± 0.02
0.5	0.50 ± 0.03	0.54 ± 0.03
1.0	1.1 ± 0.08	1.3 ± 0.10
2.0	2.1 ± 0.09	2.0 ± 0.05
10.0	10.3 ± 0.60	9.6 ± 0.40
25.0	25.4 ± 1.10	24.2 ± 1.01
50.0	53.0 ± 2.31	54.9 ± 2.01
100	105.4 ± 4.10	104.0 ± 3.50
250	254.0 ± 8.51	252.0 ± 7.00

Fig. 3. Profiles for Pu at 300.057 nm in absence and in presence of varying rare earth impurity elements. REE: Rare earths

of elements. In the present studies, close to the Pu line at 300.057 nm there are spectral lines of the elements Fe, Co, Cr, Zr, and U in the vicinity of ± 0.032 nm. Similarly, in the Pu line at 453.615 nm, there are spectral lines of Dy, Sm, U, Ti, Fe, and Ce in the vicinity of ± 0.030 nm. The presence of these elements in large amounts can result in erroneous values in the measured Pu concentration.

Spectral interferences can be corrected by determining the correction factor of each element and its concentration during the analytical run. This was done by aspirating

500 $\mu\text{g/mL}$ of individual solutions of Co, Fe, Cr, Ni, Ce, Dy, Gd, Sm, Th, and Zr to the ICP-AES to determine the contribution to the Pu signal at each of the two chosen analytical Pu lines. For instance, a 500- $\mu\text{g/mL}$ U solution gave a contribution of 11.0 $\mu\text{g/mL}$ for Pu at 300.057 nm and 6.5 $\mu\text{g/mL}$ for Pu at 453.615 nm. This would effectively imply a contribution of 0.022 μg and 0.013 μg per μg of U for the two analytical lines of Pu at 300.0567 and 453.615 nm, respectively. The relevant correction factors obtained for the two Pu analytical lines for the various ele-

ments are listed in Table V. It is clear from this table that Pu at the 300.057-nm line is less affected by rare earths but more by common metallic elements, whereas for the Pu analytical line of 453.615 nm, the reverse is true.

The results of three synthetic samples containing 10 $\mu\text{g/mL}$ Pu with varying concentrations of the interfering elements are given in Table VI. The agreement between the added and estimated amount is within 8%. Claudon et al. determined Am and Pu by ICP-AES simultaneously and also investigated the effect of U on Pu determination (11). Their results indicated that the 453.6-nm line of Pu was free from interference (error < 5%) due to the presence of U at 10 times that of Pu, while the 300.057-nm line caused an error of 10–15%. The results reported in our work (Table VI) clearly indicate that the values are within 8% once inter-element corrections are applied. However, if Pu at trace levels is to be determined in samples containing $\geq 0.005\%$ of U and Th, the ICP-AES method would have limitations in view of the complex spectra exhibited by these interfering refractory elements and, thus, prior separation of uranium/thorium would have to be applied. Based on the two lines chosen for Pu in this study, the 453.615-nm line was seen to be less prone to interference effects as compared to the Pu line at 300.057 nm.

To test the validity of the method developed, we compared the ICP-AES results with those obtained by the liquid scintillation technique and by potentiometry. The ^{241}Am concentration in the samples was ascertained using γ -spectrometry. Due corrections were applied to calculate the net Pu amount after liquid scintillation measurements. The Pu concentrations obtained for plutonium in five synthetic samples by ICP-AES/

TABLE V
Inter-element Correction Factors for Plutonium

Element (per μg)	Correction Factor for Pu		Element (per μg)	Correction Factor for Pu	
	300.057 nm	453.615 nm		300.057 nm	453.615 nm
Co	0.0076	0.0003	Dy	0.0039	0.0072
Cr	0.0011	0.0000	Ce	0.0018	0.0012
Fe	0.0190	0.0004	Gd	0.0000	0.0052
Mn	0.0005	0.0000	Sm	0.0007	0.0085
Ni	0.0105	0.0000	Th	0.0260	0.0080
U	0.0220	0.0130	Zr	0.0006	0.0007

TABLE VI
Effect of Common Impurities (Com. Imp.), U, Th, and Rare Earths on the Determination of Pu at 10 $\mu\text{g/mL}$ Concentration

Concentration of Interfering Element	Concentration of Pu Determined at:			
	300.057 nm		453.615 nm	
	Without Correction	With Correction	Without Correction	With Correction
Com. Imp. (10 $\mu\text{g/mL}$)	10.94 $\pm$ 0.52	10.60	10.24 $\pm$ 0.48	10.11
Com. Imp. (50 $\mu\text{g/mL}$)	12.20 $\pm$ 0.60	10.54	10.83 $\pm$ 0.55	10.28
Com. Imp. (100 $\mu\text{g/mL}$)	13.67 $\pm$ 0.68	10.39	11.41 $\pm$ 0.68	10.31
Uranium (10 $\mu\text{g/mL}$)	10.61 $\pm$ 0.62	10.30	10.24 $\pm$ 0.52	10.02
Uranium (50 $\mu\text{g/mL}$)	12.06 $\pm$ 0.68	10.56	10.83 $\pm$ 0.56	10.27
Uranium (100 $\mu\text{g/mL}$)	12.99 $\pm$ 0.72	10.17	11.41 $\pm$ 0.68	10.30
Thorium (10 $\mu\text{g/mL}$)	10.34 $\pm$ 0.47	10.21	10.11 $\pm$ 0.39	10.07
Thorium (50 $\mu\text{g/mL}$)	10.80 $\pm$ 0.53	10.15	10.36 $\pm$ 0.42	10.16
Thorium (100 $\mu\text{g/mL}$)	11.80 $\pm$ 0.60	10.48	10.60 $\pm$ 0.56	10.20
Rare Earths (10 $\mu\text{g/mL}$)	9.94 $\pm$ 0.47	9.92	10.30 $\pm$ 0.39	10.12
Rare Earths (50 $\mu\text{g/mL}$)	10.82 $\pm$ 0.58	10.49	11.13 $\pm$ 0.46	10.22
Rare Earths (100 $\mu\text{g/mL}$)	11.26 $\pm$ 0.68	10.60	11.98 $\pm$ 0.51	10.60

radiometry or potentiometry are given in Table VII. It should be noted that in the samples containing mg amounts of Pu only ICP-AES and the potentiometric technique could be employed since the radiometric method would involve very large dilutions. The method described in this study was regularly employed to monitor the Pu concentration in the separated samples after its removal by solvent extraction and also in radioactive waste solutions generated in our laboratory.

CONCLUSION

In this study, plutonium (Pu) was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) in the range of 0.10–100 µg/mL using the 300.057 and 453.615 nm analytical lines. The detection limit obtained for Pu is, respectively, 30 ng/mL (for 300.057 nm) and 70 ng/mL (for 453.615 nm). To test the accuracy, the results obtained by ICP-AES were compared with those obtained by radiometric and titrimetric methods. At lower concentration levels, ICP-AES showed better precision compared to the radiometric method as the latter involves very large dilutions. However, at higher concentration levels (≥ 1 mg), the titrimetric method scored over ICP-AES in terms of precision. The inter-element correction studies show that the Pu line at 453.615 nm is less prone to spectral interference effects as compare to Pu at the 300.057 nm line. It is also clear that the analysis based on Pu at the 453.615 nm line is preferable in comparison to the analysis obtained with Pu at 300.057 nm. However, this would be at the cost of an increased limit of quantification.

The method proposed is useful for the determination of Pu in aqueous waste solutions generated in radiochemical laboratories and also

TABLE VII
Comparison With Other Analytical Methods

Sample	ICP-AES (µg/mL)	Radiometric (µg/mL)	Titrimetry (µg/mL)
S-1	0.5 ± 0.13	0.6 ± 0.15	—
S-2	2.0 ± 0.09	2.2 ± 0.32	—
S-3	10.0 ± 0.08	10.2 ± 3.2	—
S-4*	240.1 ± 5.82	235.2 ± 20.21	—
S-5*	1870 ± 19.85	—	1850 ± 3.70

*Analyzed after dilution by ICP-AES/Radiometric techniques.

to monitor the trace levels of Pu left in the raffinate (after its separation with a suitable extractant) along with other metallic constituents.

ACKNOWLEDGEMENT

The authors are grateful to Dr. A. Goswami, Head, Radiochemistry Division, for his keen interest and encouragement in the course of this work. The authors are also thankful to Smt. S.K. Shiny for her help in the plutonium determination by potentiometry.

Received July 2, 2011.

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