Analytical Application of DHOA for the Determination of Trace Metallic Constituents in Pu-based Fuel Materials by ICP-AES

Arijit Sengupta*, M.J. Kulkarni, S.V. Godbole, V. Natarajan, and P.N. Pathak
Radiochemistry Division, Bhabha Atomic Research Centre,
Trombay, Mumbai 400085, India

INTRODUCTION

The performance of fuel materials in a nuclear reactor to obtain desired burn-up depends on the physical and chemical composition and constituents of the fuel materials. Because of the high neutron absorption cross-section of B, Cd, Eu, Sm, Gd, and Dy, there are stringent specification limits for fuel materials. In addition, elements that affect the physical properties of fuel, such as creep resistance, fuel density, sinterability, and hardness, also need to be monitored. Therefore, it is required to have critical quality control (both physical and chemical) of nuclear materials for their use in the reactor. Inductively coupled plasma atomic emission spectrometry (ICP-AES), which is a simultaneous, multi-elemental analytical technique with good precision and sensitivity, is regularly used for such purpose. However, the analytical technique based on ICP-AES suffers from spectral interferences. In particular, nuclear materials containing uranium, plutonium, and thorium due to their emission-rich spectra require a suitable separation procedure for removal of the major matrix without loss of analytes prior to their determination by ICP-AES. A number of separation procedures have been reported to achieve trace metal assay of nuclear materials (1–16). TBP (tri-n-butyl phosphate) has been used routinely for separation of the matrix prior to analysis. Some of the drawbacks associated with the use of TBP have been identified such as (a) non-incinera-

ABSTRACT

DHOA (di-n-hexyl-octanamide) is one of the alternative extractants to TBP (tri-n-butyl phosphate), known for the extraction of plutonium from moderate nitric acid medium without significant extraction of the fission products. The analytical application of DHOA was explored to develop a methodology for the determination of trace metallic constituents in Pu-based nuclear materials. This involved the separation of the Pu matrix by 1.1 M DHOA-dodecane, followed by the analysis of the raffinate for trace constituents by inductively coupled plasma atomic emission spectrometry (ICP-AES). A systematic study showed that five contacts of 1.1 M DHOA-dodecane were required for the quantitative extraction of Pu from 3 M HNO₃ feed for a 1-g sample size in 10 mL.

The feasibility of using DHOA for extraction of Pu from trace metallic constituents in Pu-based fuel materials without losing trace quantities of analytes of interest was studied by using synthetic samples after appropriate spiking of the common impurities and critical elements at their required specification limits (common elements: 5 ppm, critical elements: 1 ppm). A systematic study was carried out to compare the analytical performance of DHOA with TBP, which revealed that DHOA could successfully be employed for the determination of 19 trace constituents below the 5 ppm limits for common elements. The stripping performance of DHOA was also found to be better in the recovery of Pu from the loaded organic phase.

ble nature of the spent solvent yielding large volumes of secondary radioactive waste, (b) the deleterious nature of its degradation products (mainly H₂MBP and HDBP) affecting the separation and recovery, and (c) significant solubility of TBP towards the aqueous phase (17–19). In view of these drawbacks, a large number of eco-friendly N,N-dialkyl amides were explored as alternate extractants for the separation and recovery of nuclear materials from spent fuel containing minor actinides and long-lived fission products. Amongst these amides, dihexyloctanamide (DHOA) and di(2-ethylhexyl)-isobutyramide (D₂EHIBA) received considerable attention as alternate potential extractants for the reprocessing of U- and Th-based spent nuclear fuels, respectively (20).

In order to determine the applicability of these novel extractants for analytical purposes, there is a need to ascertain that these materials can extract the major matrix without loss of impurities from the raffinate even at trace levels. In case of DHOA, the extraction behavior of Pu vis-a-vis a large number of elements of analytical interest have not been well investigated. In the present study, an attempt was made to explore the application of DHOA for the separation of Pu from trace analytes. The performance of DHOA was also compared with that of TBP. These investigations have shown that 1.1 M DHOA/4 M HNO₃/dodecane can be successfully used for the extraction of Pu from an aqueous acidic solution (4M HNO₃) to bring down the concentration of Pu in the raffinate below the tolerance level (5 µg/mL) without significant loss of the con-

*Corresponding author.
arijita@barc.gov.in

stituents even at the trace level. The methodology optimized in the present case was found to be useful for the determination of 12 common impurities (CI) (Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, Zn) at 5 ppm, while seven critical elements (CE) (Ag, Eu, Sm, Gd, Dy, B, Cd) can be successfully determined at 1 ppm. Since the analytical performance of DHOA was found to be better than that of TBP, we propose that TBP can be replaced by DHOA, an environmentally benign incinerable extractant, for the determination of trace metallic constituents in a Pu matrix by inductively coupled plasma atomic emission spectrometry (ICP-AES).

EXPERIMENTAL

Instrumentation

All atomic emission spectroscopic studies were carried out using a Jobin-Yvon Ultima high resolution ICP-AES. It has the practical resolu-

tion 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.

Standard Solutions and Reagents

The standard solutions for rare earth and other common impurity elements were prepared from CertiPUR® ICP multi standard solutions (E. Merck, Darmstadt, Germany) by proper dilution with 0.5 M HNO₃. Suprapur® HNO₃ (E. Merck, Darmstadt, Germany) and quartz doubly distilled water were used for making 0.5 M HNO₃. Multi-point standardization was carried out using 0.5M HNO₃ as the lower standard and 0.05-1000 µg/mL of the corresponding elemental standard as the higher standards for each line after proper peak search. High purity PuO₂ was taken to prepare the Pu standard stock solution.

Procedure

Tracer studies were carried out with ²³⁹Pu to understand the extraction behavior of Pu in the organic phase by using 30% TBP-dodecane and 1.1 M DHOA-dodecane. The feed acidity was varied in the range of 1-6 M HNO₃. After two hours of equilibration, two phases were allowed to settle after appropriate centrifuging, followed by radiometric counting of suitable aliquots from the organic as well as the aqueous phase. A 100 mg/mL amount of Pu stock solution was prepared by dissolving appropriate amounts of high purity PuO₂ in HNO₃ medium. A 10-mL amount of stock solution was allowed to equilibrate with 1.1 M DHOA in dodecane with aqueous:organic (1:1) for two hours. Five contacts of the organic phase were given and after each contact, suitable aliquots of raffinate were analyzed for residual Pu. Similar studies were carried out using 30% TBP-dodecane as the organic phase to compare the analytical results with that of DHOA. To establish the feasibility of 1.1 M DHOA-dodecane for the separation of Pu without significant loss of impurities in the raffinate even at the trace level, studies were carried out using synthetic samples with appropriate amounts of added impurities. Five synthetic samples were prepared: (a) Pu blank (1 g of Pu dissolved in 10 mL 4 M HNO₃ medium), (b) Sample-1 (Pu blank spiked with 50 ppm of common impurities), (c) Sample-2 (Pu blank spiked with 5 ppm of common impurities), (d) Sample-3 (Pu blank spiked with 10 ppm of critical elements), and (e) Sample-4 (Pu blank spiked with 1 ppm of critical elements). All samples were subjected to solvent extraction from 4 M HNO₃ feed using 1.1 M DHOA in dodecane as the organic phase with five contacts of A:O (1:1). After proper phase separation, the raffinates were analyzed by ICP-AES against multi-standards. The same

TABLE I
Specifications and ICP-AES Operating Conditions

Spectrometer	
Optical Design	1m Czerny Turner
Grating	Holographic, ion etched optical grating
Groove Density	2400 grooves/mm
Grating Size	110 x 110 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	Cross flow and Ultrasonic type
Operating Conditions	
Ar Plasma Flow	13 L/min
Integration Time	10 s
Reflected Power	< 10 W
Sample Rate	1 ml/min

exercise was repeated using 30% TBP in dodecane as the organic phase for comparative study.

RESULTS AND DISCUSSION

To obtain optimum feed acid concentration for the effective extraction of Pu, a systematic study was carried out at various feed acidities ranging from 1 to 6 M HNO_3 . Figure 1 represents the extraction profiles of Pu at various feed acidities using 30% TBP dodecane and 1.1 M DHOA dodecane as the extracting systems. The study revealed that in the case of DHOA, the DPu value increases with an increase in feed acid molarity up to 3 M HNO_3 followed by a plateau with DPu ~20. The plateau at a higher feed acidity can be attributed to the competition of metal ions with hydronium ions (H_3O^+) getting extracted into the organic phase. A similar extraction profile was also observed for Pu with TBP but with a lower DPu value (~10) as compared to DHOA at 3M HNO_3 .

On the basis of the above study, the optimum acid concentration used in the feed solution was 3M HNO_3 for the extraction of Pu. Since the D value depends on the metal ion concentration in the feed,

it is necessary to know the number of contacts required to bring the Pu level in the raffinate down to tolerable limits (less than 5 $\mu\text{g/mL}$) in case of real samples. In view of this, a systematic study was carried out to determine the residual Pu after each contact of the organic phase with A:O (1:1). Table II represents the residual Pu in the raffinate after each contact with the organic phase, which suggested that four contacts of DHOA were required to bring the Pu concentration below tolerance limits as specified earlier, while five contacts can lead to quantitative removal of Pu. For 30% TBP, five contacts are sufficient to bring the Pu concentration down below the tolerance limit, while seven contacts are required for quantitative separation.

Based on the above experiments, it was decided to use five contacts of the organic phase for effective removal of U from the aqueous phase. An increase in DPu value was found in case of DHOA as well as TBP with increase in the number of contacts of the organic phase. The above fact can be attributed to the decrease in Pu concentration in the feed solutions after each contact. The choice of suitable extractants for the separation of the

matrix depends on the fact that the extractant system should be such that quantitative extraction of the major matrix leaves the trace constituents behind.

The analytical capacity of DHOA was explored with synthetic samples. The synthetic samples were subjected to the five contacts of 1.1 M DHOA-dodecane with A:O (1:1) from 3 M HNO_3 feed to extract Pu into the organic phase, followed by analysis of the raffinate for the elements of interest. Table III lists the analytical results of synthetic samples 1 and 2. The results implied that using the above optimized method, the elements Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, and Zn can be determined even at 5 ppm level, while Table IV lists the analytical data obtained for samples 3 and 4. Since neutron economy is of utmost importance in nuclear fuel materials, Ag, Cd, B, Eu, Sm, Gd, and Dy require stringent specification limits because of their high neutron absorption cross-sections. Our study revealed that using DHOA as an extractant, all of these critical elements could be successfully determined even at 1 ppm concentration.

Fig. 1. Extraction profile of Pu at various feed acidities using DHOA and TBP.

TABLE II
Residual Pu After Each Contact
With Organic Base

No. of Contacts	Residual Pu in the Raffinate ($\mu\text{g/mL}$)	
	1.1M DHOA	30% TBP
Initial Feed	100,000	100,000
1	5555	12500
2	292	1453
3	14	161
4	0.73	17
5	0.03	1.81
6	-	0.18
7	-	0.01

The analytical performance of DHOA was compared with that of TBP (Table V). It was found that DHOA is one of the alternative extractants to TBP for extraction of Pu into the organic phase to bring down the Pu concentration in the raffinate within the tolerable limit without significant loss of trace metallic constituents even at the trace level. The analytical performance of DHOA for the determination of trace metallic constituents in Pu-based fuel materials by ICP-AES is found to be better than with TBP and is also environmentally benign, so DHOA is preferred for analytical application.

Stripping of loaded Pu from the TBP-dodecane system is one of the major problems faced by the analytical chemist. It was observed that even after six contacts of 0.5 M HNO₃ from an aqueous phase containing 100 mg/mL of Pu, 2 µg/mL Pu is left in the organic phase, while from DHOA, five contacts of 0.5 M HNO₃ are more than enough for quantitative stripping of Pu (Table VI). Thus, not only is there a higher extraction ability, but the stripping behavior of DHOA is much more exciting than TBP.

CONCLUSION

A methodology was developed for trace metal assay of Pu-based fuel materials by ICP-AES using 1.1 M DHOA-dodecane for the chemical separation of uranium from the analytes. 1.1 M DHOA in dodecane was found to be the promising extractant for removal of Pu (five contacts, A:O = 1:1) leaving all other analytes of interest in the raffinate. The studies revealed that 5 ppm of common impurities and 1 ppm of critical elements can be determined in the Pu matrix by ICP-AES. A comparison of the analytical performance of DHOA with TBP revealed that its performance is better than that of TBP. According to the C, H, O, N principle,

TABLE III
Determination of Common Elements in Synthetic Samples Using DHOA for Matrix Separation

Element	Wave-length (nm)	Amount Added (µg/mL)	Amount Estimated (µg/mL)	Recovery (%)	Amount Added (µg/mL)	Amount Estimated (µg/mL)	Recovery (%)
Al	309.271	50	49 ± 4	98	5	5.2 ± 0.4	104
Ca	393.366	50	50 ± 2	100	5	5.1 ± 0.5	102
Co	238.892	50	47 ± 4	94	5	4.7 ± 0.6	94
Cr	283.563	50	49 ± 2	98	5	4.9 ± 0.3	98
Cu	224.7	50	51 ± 2	102	5	5.1 ± 0.4	102
Fe	259.94	50	49 ± 3	98	5	4.8 ± 0.5	96
Mg	279.553	50	53 ± 4	106	5	4.8 ± 0.4	96
Mn	257.61	50	48 ± 2	96	5	4.9 ± 0.6	98
Na	588.995	50	49 ± 3	98	5	5.1 ± 0.3	102
Ni	221.647	50	51 ± 3	102	5	5.2 ± 0.4	104
Pb	220.353	50	50 ± 4	100	5	4.7 ± 0.5	94
Zn	213.856	50	48 ± 4	96	5	5.0 ± 0.3	100

TABLE IV
Determination of Critical Elements in Synthetic Samples Using DHOA for Matrix Separation

Element	Wave-length (nm)	Amount Added (µg/mL)	Amount Estimated (µg/mL)	Recovery (%)	Amount Added (µg/mL)	Amount Estimated (µg/mL)	Recovery (%)
Ag	328.068	10	10.0 ± 0.3	100	1	1.07 ± 0.04	107
Eu	420.505	10	9.8 ± 0.4	96	1	1.2 ± 0.3	120
Sm	359.262	10	9.7 ± 0.2	94	1	0.98 ± 0.1	98
Gd	342.247	10	10.1 ± 0.5	102	1	0.97 ± 0.04	97
Dy	353.17	10	10.0 ± 0.5	100	1	0.99 ± 0.05	99
B	249.773	10	9.9 ± 0.4	98	1	1.1 ± 0.05	110
Cd	228.802	10	10.2 ± 0.9	104	1	0.98 ± 0.10	98

unlike TBP, DHOA is an incinerable, environmentally benign extractant. Therefore, it can be applied satisfactorily for removal of the Pu matrix, followed by the determination of trace metallic constituents in the raffinate by ICP-AES. The performance of DHOA was also found to be better than TBP to strip back the Pu-loaded organic phase by using 0.5M HNO₃.

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TABLE V
Analytical Data Obtained for Synthetic Samples
Using TBP and DHOA for Matrix Separation

Elements	Pu Blank (ppm)	Pu Blank + 5 ppm Cl + 1 ppm CE (ppm)	
		1.1M DHOA	30% TBP
Cr	0.3	5.5	4.7
Zn	2.9	8.3	7.1
Pb	0.5	5.2	5.3
Cd	<0.05	1.1	0.96
Ni	0.2	5.3	5.6
Co	<0.05	4.8	4.8
B	0.18	1.3	0.7
Mn	0.1	4.9	5.3
Fe	2.2	7.1	7.2
Mg	0.8	5.9	6
Al	1.7	7	6.8
Cu	0.1	4.9	5.2
Ag	<0.05	0.99	1.2
Gd	<0.05	0.97	1.1
Dy	<0.05	1.12	0.97
Sm	<0.05	1.03	0.99
Eu	<0.05	1.2	0.97
Ca	4	9.2	8.8
Na	3.2	8.1	8.4

TABLE VI
Stripping Study of the Pu-loaded Organic Phase

No. of Contacts of 0.5M HNO ₃	Residual Pu in the Organic Phase (µg/mL)	
	From 1.1M DHOA	From 30% TBP
Initial Loaded Organic	100,000	100,000
1	6000	16,666
2	240	2777
3	7.2	462
4	0.14	77
5	0.003	12
6	-	2.1

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