Determination of Trace and Ultratrace Elements in Uranium-Silicide (U_3Si_2) Fuel Employing Inductively Coupled Plasma Mass Spectrometry

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INTRODUCTION

Nuclear proliferation is one of the biggest threats to civilization, and hence, the use of highly enriched uranium ($\text{HEU} > 90\% \text{ }^{235}\text{U}$), which falls in the category of weapons-grade material, needs to be restricted. In this anticipation, the Reduced Enrichment for Research and Test Reactor (RERTR) program was initiated for the conversion of worldwide research and test reactor cores from HEU to low enriched uranium-based ($\text{LEU} < 20\% \text{ }^{235}\text{U}$) fuels (1). In order to compensate for the reduced fissile content in LEU-based fuel 'meat', extensive research and development programs have been pursued for the exploration of a fuel with maximum metal density (2-4). Though metallic uranium (U) can provide the highest achievable uranium density, its poor irradiation performance and low melting point restricts its application as a high burn-up fuel (5). The most widely accepted technical solution to overcome this limitation is the use of uranium silicide (U_3Si_2) fuel dispersed in an aluminum (Al) matrix. U_3Si_2 was found to perform extremely well even at high burn-ups (19-98% of ^{235}U in LEU) with U densities up to $\sim 5.0 \text{ g cm}^{-3}$ (2). In the Bhabha Atomic Research Centre, India, an upgradation program has been initiated for APSARA, a swimming pool type reactor, to replace the HEU fuel with LEU using plate type U_3Si_2 -Al fuel encapsulated in Al alloy cladding (1). For safe and smooth reactor operation, chemical quality control (CQC) of every

ABSTRACT

Uranium-silicide (U_3Si_2) is one of the preferred advanced nuclear fuels, having low enriched uranium ($\text{LEU} < 20\% \text{ }^{235}\text{U}$), for research and test reactors due to its numerous advantages. APSARA, a swimming pool research reactor in India, is being refurbished to replace the highly enriched uranium ($\text{HEU} > 90\% \text{ }^{235}\text{U}$) fuel with dispersion type LEU fuel (U_3Si_2 dispersed in aluminum matrix). As part of chemical quality control (CQC), a simple and effective method for the determination of trace and ultratrace elements in U_3Si_2 matrix has been developed. Thirteen trace and ultratrace elements (B, Cd, Co, Cr, Cu, Dy, Eu, Gd, Mg, Mn, Ni, Sm, and V) were quantitatively separated from the U_3Si_2 matrix and determined by inductively coupled plasma mass spectrometry (ICP-MS). The matrix element, silicon (Si), was separated as its volatile fluoride (silicon tetrafluoride, SiF_4), whereas uranium (U) was separated by conventional tributylphosphate (TBP) in carbon tetrachloride (CCl_4) medium. Recovery studies employing the standard addition technique followed by ICP-MS analysis were applied to validate the proposed methodology. An independent tracer technique with ^{51}Cr and $^{152+154}\text{Eu}$ tracers was also employed to enhance the confidence in the proposed separation method. The instrument detection limit (IDL) and the method detection limit (MDL) for the 13 analytes were found in the range of $6\text{--}700 \text{ ng L}^{-1}$ and $8\text{--}200 \text{ } \mu\text{g kg}^{-1}$, respectively. Three real U_3Si_2 samples were analyzed, employing the proposed method, with the %RSD deviation ranging between 3-9% (1σ).

nuclear material is essential. The presence of some trace metallic and non-metallic elements in the nuclear fuel can affect the optimum performance of a reactor (6, 7). These trace elements which get incorporated in nuclear fuel either from the precursors or during various fuel fabrication steps, need to be quantified precisely and accurately. The available methods for the determination of trace metallic elements in various nuclear materials are inductively coupled plasma mass spectrometry (ICP-MS) (8-12), inductively coupled plasma atomic emission spectrometry (ICP-AES) (13,14), flame atomic absorption spectroscopy (FAAS) (15,16), ion chromatography (IC) (17,18), etc. Among all these techniques, ICP-MS is the most versatile multi-elemental technique with rapid analysis, high sample throughput, long linear calibration range, low detection limit, and fewer spectroscopic interferences, etc. (19-22). For ICP-MS analysis, it is recommended to analyze solutions with total dissolved solid content $\leq 0.1\%$. Whenever the analyte concentration in the matrix is in the trace/ultratrace level, it is necessary to separate the matrix prior to quantification by ICP-MS as only dilution may bring down the analyte concentration below the detection limit of the instrument. A matrix separation procedure was developed to quantitatively separate 13 analytes (B, Cd, Co, Cr, Cu, Dy, Eu, Gd, Mg, Mn, Ni, Sm, and V) from the U_3Si_2 matrix, followed by their quantification by ICP-MS.

The matrix element, silicon, was removed as its volatile compound (SiF_4) in the presence of HNO_3/HF . This process was carried out in the presence of mannitol to prevent

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loss of boron (23,24). The other matrix element, uranium, was separated by conventional solvent extraction using tributylphosphate (TBP) in carbon tetrachloride (CCl_4) (7). The raffinate was analyzed by ICP-MS employing the external calibration technique. Recovery studies employing the standard addition technique followed by ICP-MS analysis were carried out to validate the developed methodology (25). The separation procedure was cross-validated by an independent tracer technique by adding carrier-free ^{51}Cr and $^{152+154}\text{Eu}$ tracers before any chemical treatment and finally analyzing the raffinate by gamma spectrometry (25). Three real U_3Si_2 samples were analyzed for trace and ultratrace elements by the developed method.

EXPERIMENTAL

Instrumentation

Inductively Coupled Plasma Mass Spectrometer

An ICP-orthogonal acceleration time of flight mass spectrometer (ICP-oe-TOF-MS), Model Optimass 8000R (GBC, Australia), was used for the determination of trace and ultratrace elements in U_3Si_2 matrix. Details of the instrumental and operating parameters are given elsewhere (25).

Gamma Spectrometer

A 3"X3" NaI (TI) well-type detector coupled to a Multichannel Analyzer (Electronic Corporation of India Limited) was used to study the percentage recovery of the tracers (^{51}Cr and $^{152+154}\text{Eu}$) in the final raffinate. The detector has a resolution of 46.2 KeV (FWHM) at 661 KeV. Carrier-free activities of ^{51}Cr and $^{152+154}\text{Eu}$ were monitored at 320 KeV and 122 KeV, respectively.

Reagents and Solutions

Suprapur® HNO_3 and HF (Merck, Darmstadt, Germany), TBP (Merck), and CCl_4 (Merck) were used for sample preparation. De-ionized water, obtained from a Milli-Q® system (18M Ω , Millipore Corporation, Bedford, MA, USA) was used for dilution. The ICP standards of 1000 mg L $^{-1}$ (BDH, UK) were diluted appropriately to prepare multi-element standard solutions. Two carrier-free radio tracers, ^{51}Cr and $^{152+154}\text{Eu}$, were obtained from the Board of Radiation and Isotope Technology (BRIT), India. Eppendorf® micropipettes, Nalgene® PP measuring flask and funnels, and Teflon® PFA beakers were used throughout the experiment.

Dissolution and Matrix Separation

About 1.0 g of U_3Si_2 was taken in a Teflon beaker with 10 mL concentrated HNO_3 and 1 mL of 100 mg L $^{-1}$ manitol solutions. The mixture was then placed under an IR lamp, and concentrated HF was added dropwise until the solution became clear. The solution was then evapo-

rated to near dryness and brought into 10 mL 4M HNO_3 medium. Uranium was then separated from the solution by three contacts with 20 mL 30% TBP in CCl_4 (O/A = 2). The raffinate was again evaporated to near dryness and made up to 25 mL volume in 1% (v/v) HNO_3 medium for ICP-MS analysis.

Choice of Nuclides

In mass spectrometric analysis, selection of a suitable nuclide is necessary so as to have better sensitivity, low detection limit, and minimum or no isobaric/polyatomic interferences. The nuclides of the elements chosen for our study are listed in Table I, along with their natural abundances and possible interferences.

Recovery Studies by ICP-MS Employing Standard Addition Technique

Almost equal amounts (~1.0 g) of a real U_3Si_2 sample from the same batch were taken in four Teflon beakers. One of these was considered as a sample blank, and standard addition was carried out in the other three samples. Individual

TABLE I
List of Nuclides Monitored During Mass Spectrometric Analysis

No.	Monitored Nuclides	Abundance (%)	Possible Interferences
1	^{11}B	80.2	—
2	^{114}Cd	28.73	^{114}Sn , $^{98}\text{Mo}^{16}\text{O}$, $^{98}\text{Ru}^{16}\text{O}$
3	^{59}Co	100	—
4	^{52}Cr	83.8	—
5	^{63}Cu	69.17	$^{47}\text{Ti}^{16}\text{O}$
6	^{163}Dy	24.97	$^{147}\text{Sm}^{16}\text{O}$
7	^{153}Eu	52.2	$^{137}\text{Ba}^{16}\text{O}$
8	^{57}Fe	2.2	—
9	^{160}Gd	21.86	$^{144}\text{Nd}^{16}\text{O}$, $^{144}\text{Sm}^{16}\text{O}$, ^{160}Dy
10	^{24}Mg	78.9	—
11	^{55}Mn	100	—
12	^{60}Ni	26.1	—
13	^{152}Sm	26.7	^{152}Gd , $^{138}\text{Ba}^{14}\text{N}$
14	^{51}V	99.75	—

1000 mg L⁻¹ elemental standards of the analytes were added to the samples after appropriate dilution. All four samples were then treated in the same manner as discussed above and finally analyzed by ICP-MS. The results of these recovery studies are summarized in Table II.

Recovery Studies by Y-Spectrometry Employing ⁵¹Cr and ¹⁵²⁺¹⁵⁴Eu Tracers

Recovery study by Y-spectrometry is a unique technique to validate any proposed separation procedure as it permits no blank correction on the spiked amount. However, unavailability or restricted availability of radiotracers limits the applicability of this technique. In our case, we used carrier-free ⁵¹Cr and ¹⁵²⁺¹⁵⁴Eu tracers to validate the separation procedure mainly for transition and rare earth elements. One stock solution of each tracer was prepared by adding the tracer to the individual solution containing natural Cr and Eu, respectively. The specific activities of these solutions were in the range 1.0–3.0 x 10⁵ CPM mL⁻¹. The concentration of the chromium solution was 25 µg mL⁻¹ and that of europium was 1 µg mL⁻¹. A 0.25 mL aliquot of these stock solutions was mixed in a counting tube, and the volume was made up to 2.5 mL with 4M HNO₃ which would serve as reference. Then, 1 mL stock solution of both tracers was mixed with ~1.0 g of U₃Si₂ and chemically treated in the same manner as discussed earlier. Finally, the raffinate was made up to 10.0 mL in 4M HNO₃ medium. In a counting tube, 2.5 mL of this solution was taken, and both the counting tubes (reference and sample) were counted for ⁵¹Cr at 320 KeV and for ¹⁵²⁺¹⁵⁴Eu at 122 KeV. The results of the recovery studies are listed in Table III.

RESULTS AND DISCUSSION

The real U₃Si₂ samples were first qualitatively analyzed by ICP-MS which revealed the presence of only 12 elements (B, Cd, Co, Cr, Dy, Eu, Gd, Mg, Mn, Ni, Sm, and V) having specifications in the nuclear fuel. Also other elements like Cu and Fe which have specifications in the fuel, but not detected in the real samples, were also considered in the recovery studies. The developed separation procedure ensures quantitative recoveries of the 13 elements (B, Cd, Co, Cr, Cu, Dy, Eu, Gd, Mg, Mn, Ni, Sm, and V) and reduces the total U matrix content to < 20 µg mL⁻¹ thereby yielding a decontamination factor of ~ 10³. For the determination of iron, intensity at mass number 57 was monitored due to the presence of isobaric interferences at mass number 54 (⁴⁰Ar¹⁴N) and 56 (⁴⁰Ar¹⁶O). However, due to the low abundance of ⁵⁷Fe, the results were highly irreproducible and hence, iron is not reported. The quantitative removal of Si as its volatile fluoride compound was confirmed by monitoring the separated solutions by ICP-AES. Mannitol was added prior to the sample dissolution step to prevent loss of boron on heating and the consequent HF addition step (23,24). The formation of an ester between either B(OH)₃ or BF₄⁻ (Lewis acid) and the mannitol (Lewis base) causes the retention of B in the solution. Addition of HF was done slowly to remove most of the Si as silicon tetrafluoride (SiF₄) because in the presence of excess HF, SiF₄ gets converted into water-soluble hexafluoro silicic acid (H₂SiF₆). Table I lists the monitored nuclides along with their natural abundances and possible interferences. A 10 µg L⁻¹ solution of individual analytes, which are responsible for polyatomic interferences on the monitored nuclides, were analyzed. It was found that other than oxide ions of Ba and rare earth elements, the signals for other poly-

atomic species were less than the detection limit. It has been reported in the literature that in the case of REEs the oxide ion formation yield (MO⁺/M⁺) of the interfering species, relevant to the present study, are very low (26). Therefore, considering the low concentration of REEs (present in the sub-ppm range) and no detectable Ba in U₃Si₂, the individual analyte intensities were only considered without applying any polyatomic interference correction equations. It can be seen that only ¹¹⁴Cd, ¹⁶⁰Gd, and ¹⁵²Sm have isobaric interferences from ¹¹⁴Sn (0.65%), ¹⁶⁰Dy (2.34%), and ¹⁵²Gd (0.2%), respectively. The intensity of ¹¹⁸Sn (abundance = 24.22%) was monitored in actual sample solutions and was found to be the same as that of the blank value. Since the blank-corrected intensities were considered for every element throughout the analysis, the interference of ¹¹⁴Sn on ¹¹⁴Cd was consequently taken care of. The interference of ¹⁶⁰Dy and ¹⁵²Gd on ¹⁶⁰Gd and ¹⁵²Sm, respectively, was taken care of by applying the following interference correction equations:

$$I_{160\text{Gd}}^{\text{act}} = I_{160}^{\text{obs}} - (I_{163\text{Dy}}^{\text{act}} \times \frac{2.34}{24.97})$$

and

$$I_{152\text{Sm}}^{\text{act}} = I_{152}^{\text{obs}} - (I_{158\text{Gd}}^{\text{act}} \times \frac{0.2}{24.84})$$

where I^{act} and I^{obs} are the actual intensity of the analyte and the observed intensity at a particular mass number, respectively.

Because of the unavailability of matrix-matched SRMs containing the analytes of interest, recovery studies by standard addition were applied for method validation using a real sample of U₃Si₂. Individual analyte standards of all the elements of interest were used in the standard addition method and their concentration was varied near their specification limit in the fuel. These specification limits were

TABLE II
Results of Recovery Studies (Sample Amount: ~ 1.0 g, Volume = 25 mL, N = 10)

Ana-lytes	Specifi-cation Limit ($\mu\text{g g}^{-1}$)	Amount Added (μg)	Amount Found (μg)	Recovery (%)	Ana-lytes	Specifi-cation Limit ($\mu\text{g g}^{-1}$)	Amount Added (μg)	Amount Found (μg)	Recovery (%)
B	5	0	1.92±0.07	—	Gd	< 3 ^b	0	ND	—
		2.5	4.44±0.14	101±6			1	1.10±0.10	110±9
		5	6.75±0.22	97±5			2	2.04±0.13	102±6
		10	11.7±0.4	98±4			3	2.95±0.18	98±6
Cd	2	0	—	—	Mg ^a	50	0	15.4±0.42	—
		1	1.08±0.08	108±7			25	39.5±1.2	96±5
		2	1.96±0.11	98±6			50	64.7±2.0	99±4
		4	3.92±0.20	98±5			100	115.2±3.2	100±3
Co	10	0	4.46±0.13	—	Mn	10	0	2.83±0.14	—
		5	9.55±0.32	102±7			5	7.65±0.33	96±7
		10	14.4±0.8	99±8			10	12.6±0.5	98±5
		20	24.3±1.2	99±6			20	22.7±0.7	99±4
Cr ^a	25	0	14.2±0.6	—	Ni ^a	25	0	12.4±0.56	—
		12.5	26.8±1.1	101±10			12.5	24.6±1.1	98±10
		25	38.1±1.6	96±7			25	37.2±1.4	99±6
		50	64.2±2.4	100±5			50	62.6±2.3	100±5
Cu ^a	50	0	ND	—	Sm	< 3 ^b	0	0.28±0.02	—
		25	23.6±1.4	94±6			0.5	0.76±0.04	96±9
		50	49.5±2.1	99±4			1.5	1.77±0.06	99±4
		100	97.3±3.1	97±3			3	3.25±0.13	99±4
Dy	< 3 ^b	0	ND	—	V	10	0	6.60±0.20	—
		1	0.92±0.04	92±4			5	11.3±0.3	94±7
		2	2.04±0.10	102±5			10	16.9±0.5	103±5
		3	2.92±0.12	97±4			20	26.4±0.8	99±4
Eu	< 3 ^b	0	ND	—					
		1	1.00±0.05	100±5					
		2	1.98±0.06	99±3					
		3	3.10±0.16	103±5					

^a Determined by further diluting 1 mL of the solution into 10 mL.

^b Total rare earth element concentration should be less than 3 $\mu\text{g g}^{-1}$.

ND: Not detected.

TABLE III
Results of Recovery Studies by Y-Spectrometry (N=10, 60 s Counting)

	Counts for ⁵¹ Cr at 320 KeV	Recovery (%)	Counts for ¹⁵²⁺¹⁵⁴ Eu at 122 KeV	Recovery (%)
Reference	35776±248	—	55010±250	—
Sample-1	34854±160	97±1	54130±170	98±1
Sample-2	34694±200	97±1	54500±200	99±1
Sample-3	34900±225	98±1	53900±250	98±1
Sample-4	34540±180	97±1	54710±300	100±1
Sample-5	34750±210	97±1	54020±280	98±1

arrived at by the experience gained from the fuel performance of thermal and research reactors. Analysis of the four solutions, one of which was considered as sample blank and the other three spiked with different concentrations of the analytes, by ICP-MS results in $\geq 92\%$ recovery for the 13 individual analytes, as shown in Table II. The precision indicated in the table is the overall precision calculated by propagation of error, taking into account both the external ($N=2$) as well as the internal ($N=5$) standard deviation. To enhance our confidence in the separation procedure, recovery studies were also carried out by an independent tracer technique. The results of this exercise are shown in Table III where it can be seen that the recovery of both Cr and Eu is $\geq 97\%$, thereby cross-validating the proposed method for transition metals and REEs.

Detection Limits

Both the instrument detection limits (IDLs) and the method detection limits (MDLs) were determined for all 13 elements as per the reported procedure (27-29). The

IDLs were obtained by analyzing the 1% (v/v) pure HNO_3 solution. For the MDL determination, the discussed separation procedure was followed exactly in the absence of the sample, and the solutions were analyzed by ICP-MS. The 3σ values of the IDLs and the MDLs are tabulated in Table IV.

Analysis of the Samples

Three real U_3Si_2 samples were analyzed by the proposed method, and the results are listed in Table V. It can also be seen from this table that all of the 13 elements are present well below their respective specification limits in the fabricated fuel. The relative standard deviation (1σ) of the analytes in these samples varied between 3–9%.

CONCLUSION

The proposed method effectively separates all 13 elements (B, Cd, Co, Cr, Cu, Dy, Eu, Gd, Mg, Mn, Ni, Sm, and V) from the U_3Si_2 matrix, which could then be quantified precisely and accurately by ICP-MS. The developed separation procedure reduces the matrix concentration to $< 20 \text{ mg L}^{-1}$ in the

final solution for ICP-MS analysis. The methodology was validated by the standard addition technique, using ICP-MS, with recoveries of $\geq 92\%$ for all of the elements of interest. An independent tracer technique was also used to cross-validate the method. Three real U_3Si_2 samples were analyzed by this developed procedure. The method provides a simple and efficient way of analyzing trace and ultra trace elements in U_3Si_2 fuel.

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TABLE IV
IDL and MDL of All the Analytes (N=5)

Elements	IDL (ng L^{-1})	MDL ($\mu\text{g kg}^{-1}$)
B	700	200
Cd	40	10
Co	30	25
Cr	75	8
Cu	42	51
Dy	10	20
Eu	6	10
Gd	14	24
Mg	20	25
Mn	25	15
Ni	200	60
Sm	20	30
V	25	10

TABLE V
Results of Analysis of Three Real U_3Si_2 Fuel for Metals by ICP-MS

Elements	Sample 1 ($\mu\text{g g}^{-1}$)	Sample 2 ($\mu\text{g g}^{-1}$)	Sample 3 ($\mu\text{g g}^{-1}$)
B	2.23 ± 0.12	1.84 ± 0.08	2.45 ± 0.14
Cd	0.13 ± 0.01	ND	0.16 ± 0.01
Co	4.84 ± 0.1	7.34 ± 0.22	6.85 ± 0.6
Cr	10.5 ± 0.5	13.7 ± 0.6	12.6 ± 0.3
Cu	ND	ND	ND
Dy	ND	0.33 ± 0.02	0.54 ± 0.02
Eu	0.27 ± 0.02	0.23 ± 0.01	0.37 ± 0.02
Gd	ND	0.16 ± 0.01	0.12 ± 0.01
Mg	13.5 ± 0.4	11.6 ± 0.5	12.7 ± 0.4
Mn	3.47 ± 0.1	2.92 ± 0.15	4.67 ± 0.20
Ni	17.5 ± 0.6	10.7 ± 0.4	13.6 ± 0.6
Sm	0.66 ± 0.02	0.35 ± 0.02	ND
V	3.62 ± 0.2	4.54 ± 0.22	3.53 ± 0.12

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