Development of an Analytical Methodology for the Determination of Trace Metal Constituents in U-Zr Alloy by ICP-AES

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INTRODUCTION

Uranium-based binary and ternary alloy fuels are possible candidates for use in advanced fast spectrum reactors (1-4). Amongst these, U-Zr and U-Pu-Zr alloys, owing to their higher heavy atom density, are considered to be potential alloy fuels for meeting the desired burn-up, high breeding ratio (~1.4), lower doubling time, and high thermal conductivity (5-16). Several studies have been carried out to understand the thermo-physical, mechanical, and metallurgical properties of U-Zr and U-Pu-Zr alloy samples (17-28).

The performance of any fuel in the reactor depends on purity, chemical and physical properties, and isotopic compositions of the constituents of the fuel. Therefore, stringent chemical quality control and quality assurance programs are required to meet the specifications of the fuel as set by the fuel designer before its use in the reactor. Hence, development of a suitable analytical methodology for the estimation of trace constituents in uranium-zirconium (U-Zr) alloy becomes a pre-requisite.

Inductively coupled plasma atomic emission spectrometry (ICP-AES), known for its simultaneous multi-element detection capabilities with improved precision, sensitivity, and detection limits has been extensively used as an analytical technique for trace metal assay of nuclear materials (29-41). The present study features the first work of its kind for the trace metal assay of U-Zr alloy samples after chemical

ABSTRACT

Since uranium-zirconium (U-Zr) alloys are one of the advanced fuels for future fast reactors, it is desirable to develop a method for the determination of trace constituents in U-Zr alloys as an integral part of chemical quality control of nuclear materials.

A methodology was developed involving the simultaneous and selective extraction of U and Zr into the organic phase containing 30% tributyl phosphate (TBP)-CCl₄, followed by the analysis of the raffinate for trace metallic constituents by inductively coupled plasma atomic emission spectrometry. The extraction profiles of U and Zr at various feed nitric acid concentrations revealed that 7M HNO₃ was the optimum feed acidity for the simultaneous extraction of U and Zr using 30% TBP-CCl₄ as the organic phase.

Due to the emission-rich spectra of U and Zr, a systematic study on the spectral interferences of U and Zr on the analytes of interest was carried out which revealed that 10 µg/mL of U and 1000 µg/mL of Zr can be tolerated by the specified analytical wavelengths for the trace level determination of these analytes. Five sequential extractions of 30% TBP-CCl₄ were found to be sufficient to bring down the residual matrix concentration in the raffinate within tolerable limits.

The methodology developed was validated using synthetic samples and found to be satisfactory for the 16 analytes of interest (Al, B, Cd, Co, Cr, Cu, Dy, Eu, Gd, Fe, Mn, Na, Ni, Sm, and Zn), including common impurities and rare earth elements (REEs), even at trace levels.

separation of U and Zr, followed by analyte determination in the raffinate using ICP-AES. Both U and Zr, the major constituents of the alloy, have line-rich emission spectra which can lead to spectral interferences during trace metal assay. Therefore, prior chemical separation of the major matrix is a pre-requisite for the determination of trace level metal impurities by ICP-AES. Generally, for uranium-based nuclear materials, the trace metal determination by ICP-AES is carried out after chemical separation of U using solvent extraction from HNO₃ medium, followed by the analysis of the raffinate (30-38). Huff et al. (42) attempted to determine the trace metal impurities in U-Pu-Zr alloy fuel using anion exchange partition chromatography.

In the present work, a methodology for the determination of trace metal constituents in U-Zr alloy was developed by ICP-AES, involving optimization of a method for the simultaneous removal of U and Zr by solvent extraction using 100 mL of 30% TBP/70%CCl₄/HNO₃ (1:1), followed by the determination of the trace metals in the raffinate. A systematic study was also carried out to understand the effect of residual U and Zr on the determination of the analytes at trace levels which revealed that 10 µg/mL of U and 1000 µg/mL of Zr can be tolerated for the estimation of 16 impurities at trace levels (Al, B, Cd, Co, Cr, Cu, Dy, Eu, Gd, Fe, Mn, Na, Ni, Sm, and Zn).

The methodology was validated using synthetic samples by adding known amounts of impurities to solutions with known U-Zr compositions. The study was further extended to four real samples. The

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methodology was found to be suitable for the determination of trace metal constituents in U-Zr alloy samples.

EXPERIMENTAL

Instrumentation

A Jobin-Yvon Model Panorama axial-view ICP spectrometer, equipped with a polychromator with 35 fixed analytical channels and limited sequential facility to select any analytical line within 2.2 nm of the polychromator lines, was used (Jobin-Yvon, Longjumeau, France). 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 was 0.028 nm. The main instrumental operating conditions are given in Table I.

Preparation of Standards and Samples

Suprapur® acids (E. Merck, Darmstadt, Germany) and quartz doubly distilled water were used for preparation of the standards and sample solutions. Multi-element standard solutions were prepared from commercially available SpecPure® solutions (Johnson-Matthey Chemicals Ltd., London, UK) using appropriate dilution with 0.5 M HNO₃. These solutions were used for obtaining calibration plots during ICP-AES analysis. A multi-point standardization was carried out using 0.5 M HNO₃ as the blank and 0.5, 10, 20, 50, and 100 µg/mL of the corresponding elemental standard as the higher standards, respectively. High purity U₃O₈ and SpecPure Zr solutions were taken to prepare solutions in the concentration range of 100–1000 µg/mL to monitor the contribution of U and Zr on the various analyte wavelengths. Similarly, 0.5 M HNO₃ served as a reagent blank to monitor any contribution arising from the blank.

Procedure

To optimize the methodology for the simultaneous extraction of U and Zr, a systematic study was carried out to obtain the extraction profile by varying the feed HNO₃ concentration in the range of 1–8 M using 30% TBP in CCl₄ as the organic phase. Five sequential extractions using 100 mL of 30%TBP/70%CCl₄ with an aqueous:organic phase (A:O) ratio of 1:1 were found to be sufficient for bringing the residual matrix in the raffinate within the tolerance limits. These are the maximum concentrations of the matrix which will not affect the trace level determinations (10 µg/mL for U and 1000 µg/mL for Zr).

The method was validated using synthetic samples. One gram each of various U-Zr alloy samples were dissolved in 10 mL of a 0.05% HF-HNO₃ mixture (HF 0.005 mL and HNO₃ 9.995 mL). Uranium and Zr

were separated simultaneously from 7M HNO₃ using five extractions of 30% TBP in 70% CCl₄ in a ratio A:O= 1:1, followed by the analysis of the raffinate (10 mL for trace constituents).

RESULTS AND DISCUSSION

Spectral Interference of U and Zr on Specified Analytical Channels

SpecPure U and Zr solutions were fed to the instrument independently at various concentrations to monitor the specified analytical channels and to understand the spectral interference due to the matrix. It is required that U as well as Zr are determined along with the other analytes to obtain correction factors at specified concentration levels. The 385.958 nm and 342.823 nm lines were chosen for the U and Zr determinations, respectively. The interference studies revealed that the effects of U on

TABLE I
Specifications and Operating Conditions of ICP-AES

Spectrometer	
Optical design	1 m Czerny Turner
Grating	Holographic, 2 ion-etched optical gratings
Groove density	2400 grooves/mm, 4320 grooves/mm
Grating size	110X110 mm
Wavelength range	120–800 nm
Bandpass	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 concentric
Operating Conditions	
Operating power	1 kW
Ar plasma flow	13 L/min
Integration time	10 s
Reflected power	<10 W
Sample rate	1 mL/min

TABLE II
Spectral Interference of Uranium
on Analytes of Interest

Elements	Wave-length (nm)	Contribution from U to the Specified Analytical Lines		
		U (10 µg/mL)	U (100 µg/mL)	U (1000 µg/mL)
Al	308.2	0.19	1.9	18.6
B	249.6	< 0.05	0.21	2.4
Ca	396.8	< 0.05	< 0.05	0.10
Cd	228.8	< 0.05	< 0.05	0.19
Co	237.8	< 0.05	0.17	1.5
Cr	205.5	< 0.05	< 0.05	0.15
Cu	324.7	< 0.05	0.26	2.0
Dy	353.1	< 0.05	0.07	0.60
Eu	381.9	< 0.05	< 0.05	0.16
Gd	342.2	< 0.05	0.22	1.9
Fe	259.9	< 0.05	0.13	0.97
Mn	257.6	< 0.05	< 0.05	0.23
Na	589.5	< 0.05	0.26	2.7
Ni	232	< 0.05	0.24	2.6
Sm	359.2	< 0.05	0.3	3.2
Zn	213.8	< 0.05	< 0.05	0.11

TABLE III
Spectral Interference of Zirconium
on Analytes of Interest

Elements	Wave-length (nm)	Contribution from Zr to the Specified Analytical Lines		
		Zr (100 µg/mL)	Zr (500 µg/mL)	Zr (1000 µg/mL)
Al	308.2	<0.05	<0.05	<0.05
B	249.6	<0.05	<0.05	<0.05
Ca	396.8	<0.05	<0.05	<0.05
Cd	228.8	<0.05	<0.05	<0.05
Co	237.8	<0.05	0.15	0.32
Cr	205.5	<0.05	<0.05	<0.05
Cu	324.7	<0.05	<0.05	0.07
Dy	353.1	<0.05	<0.05	<0.05
Eu	381.9	<0.05	<0.05	<0.05
Gd	342.2	<0.05	<0.05	0.09
Fe	259.9	<0.05	<0.05	<0.05
Mn	257.6	<0.05	<0.05	<0.05
Na	589.5	0.07	0.45	0.87
Ni	232	<0.05	<0.05	0.09
Sm	359.2	<0.05	<0.05	0.07
Zn	213.8	<0.05	<0.05	< 0.05

the specified analytical lines were more pronounced in comparison to Zr. In case of U, a 10 µg/mL concentration of U was found to be tolerable for the trace determination of the analytes of interest at specified lines, except for Al, which needs to be corrected (for 308.20 nm line) with 0.19 µg/mL per µg/mL of U (Table II). For Zr, 1000 µg/mL of Zr can be tolerated for most of the specified analytical lines at trace level determination, except for Co at 237.80 nm and Na at 589.50 nm (Table III). For the above two lines (Co at 237.80 nm and Na at 589.50 nm), 100 µg/mL of Zr is the limit of tolerance.

Optimization of Methodology

The variation of distribution (D) coefficients D_U and D_{Zr} for U and Zr with variations in feed HNO_3 concentration are shown in Figure 1. It was found that the D_U value increased with an increase in acidity and attained a plateau beyond

Fig. 1. Extraction profile of U and Zr in various feed acidity.

6 M with $D_U \sim 44$, while D_{Zr} increased beyond 4 M and leveled off at 7 M acidity with $D_{Zr} \sim 3.3$. This suggested that for the simulta-

neous extraction of U and Zr from U-Zr alloy, 7M feed acidity would be optimum for matrix separation using the TBP- CCl_4 system. System-

TABLE IV
Analytical Data Obtained for
Synthetic Sample #1 (U-2% Zr)

Elements	Synthetic Sample With the Composition of U-2%Zr With Known Amounts of Added Elements		
	Added (µg/mL)	Estimated (µg/mL)	Recovery (%)
Al	0.5	0.40 ± 0.04	80
B	0.5	0.52 ± 0.05	104
Ca	0.5	0.58 ± 0.07	116
Cd	0.5	0.44 ± 0.04	88
Co	0.5	0.42 ± 0.04	84
Cr	0.5	0.49 ± 0.03	98
Cu	0.5	0.45 ± 0.04	90
Dy	0.5	0.45 ± 0.04	90
Eu	0.5	0.48 ± 0.04	96
Gd	0.5	0.46 ± 0.05	92
Fe	0.5	0.52 ± 0.05	104
Mn	0.5	0.50 ± 0.04	100
Na	0.5	0.51 ± 0.04	102
Ni	0.5	0.47 ± 0.04	94
Sm	0.5	0.48 ± 0.05	96
Zn	0.5	0.49 ± 0.04	98

atic studies revealed that five contacts of 30% TBP-CCl₄ with A:O=1:1 is required to make the concentration of U and Zr in the raffinate at tolerable limits.

Analysis of Synthetic and Real Samples for the Determination of Trace Metals

Synthetic samples were prepared with the composition of U-2%Zr (synthetic sample #1), U-6%Zr (synthetic sample #2), and U-10%Zr (synthetic sample #3), and adding known amounts (5 µg/mL) of the analytes of interest. After separation of the major matrix below tolerable limits, the raffinate was analyzed for 16 trace metal constituents (Tables IV, V, and VI). It was observed that for most of the elements the % recovery was satisfactory. For Ca and B (which are common contaminants), an increase in estimated value might be due to process pickup.

Four real samples (obtained from the Radiometallurgical Division, Bhabha Atomic Research Centre, Trombay, India) were analyzed having the composition of U-10%Zr, U-6%Zr, U-2%Zr, and U-metal using the optimized method (five contacts of 30%TBP/70%CCl₄, A:O=1:1, to bring U and Zr in the raffinate below the tolerance level, followed by determination of the trace constituents in the raffinate. It was found that Cr, Mn, Ni, and Cu were present in the U metal and in U-2%Zr, while Zn and Fe were present in all of the samples, except for U-10%Zr. All of the critical elements (Eu, Sm,

TABLE V
Analytical Data Obtained for
Synthetic Sample #2 (U-6% Zr)

Elements	Synthetic Sample With the Composition of U-6%Zr With Known Amounts of Added Elements		
	Added (µg/mL)	Estimated (µg/mL)	Recovery (%)
Al	0.5	0.41 ± 0.04	82
B	0.5	0.58 ± 0.05	116
Ca	0.5	0.58 ± 0.07	116
Cd	0.5	0.46 ± 0.04	92
Co	0.5	0.47 ± 0.04	94
Cr	0.5	0.42 ± 0.03	84
Cu	0.5	0.41 ± 0.04	82
Dy	0.5	0.41 ± 0.04	82
Eu	0.5	0.40 ± 0.04	80
Gd	0.5	0.49 ± 0.05	98
Fe	0.5	0.52 ± 0.05	104
Mn	0.5	0.40 ± 0.04	80
Na	0.5	0.43 ± 0.04	86
Ni	0.5	0.47 ± 0.04	94
Sm	0.5	0.46 ± 0.05	92
Zn	0.5	0.42 ± 0.04	84

TABLE VI
Analytical Data Obtained for
Synthetic Sample #3 (U-10% Zr)

Elements	Synthetic Sample With the Composition of U-10%Zr With Known Amounts of Added Elements		
	Added (µg/mL)	Estimated (µg/mL)	Recovery (%)
Al	0.5	0.44 ± 0.04	88
B	0.5	0.55 ± 0.05	110
Ca	0.5	0.54 ± 0.07	108
Cd	0.5	0.46 ± 0.04	92
Co	0.5	0.48 ± 0.04	96
Cr	0.5	0.42 ± 0.03	84
Cu	0.5	0.40 ± 0.04	80
Dy	0.5	0.45 ± 0.04	90
Eu	0.5	0.43 ± 0.04	86
Gd	0.5	0.47 ± 0.05	94
Fe	0.5	0.42 ± 0.05	82
Mn	0.5	0.50 ± 0.04	100
Na	0.5	0.53 ± 0.04	106
Ni	0.5	0.47 ± 0.04	94
Sm	0.5	0.45 ± 0.05	90
Zn	0.5	0.45 ± 0.04	90

Gd, Dy, and Cd) were found to be below the limits of detection, except B, which was found to be present in the U-2%Zr and U-6%Zr samples. The overall impurities were found to be 6.2, 23, 284.5, and 83.9 ppm in U-10%Zr, U-6%Zr, U-2%Zr, and U metal, respectively.

CONCLUSION

Attempts were made to develop a method for the determination of trace metal constituents in uranium-zirconium (U-Zr) alloy samples. The contribution of U and Zr on the commonly used analytical lines of the analytes of interest suggested that 10 µg/mL of U and 1000 µg/mL of Zr can be tolerated in the aqueous phase after extraction. Extraction profiles of U and Zr with varying HNO₃ molarity indicated that for the simultaneous extraction of U and Zr from the feed to the tolerable concentrations in the raffinate, five sequential extractions of 30% tributyl phosphate (TBP)/70%CCl₄ (A:O=1:1) and a feed acidity of 7M HNO₃ were required.

This method was successfully applied to the determination of 16 trace metal constituents (Al, B, Cd, Co, Cr, Cu, Dy, Eu, Gd, Fe, Mn, Na, Ni, Sm, and Zn) in U-Zr alloy samples and was validated using synthetic samples.

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