Direct Determination of Cadmium in Uranium-Zirconium-based Metallic Fuel Using GFAAS: An Insight Into the Effect of Matrix on the Atomization of Cadmium

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INTRODUCTION

Uranium- and plutonium-based nuclear fuels are required to conform to stringent specifications as regards the trace metallic constituents since they have an important bearing on fuel performance. Trace metals, such as B, Cd, and Gd in particular amongst the rare earths, have a very high neutron absorption cross-section which in turn can affect the neutron economy of the reactor fuel (1,2). Cadmium is one such element to be monitored in the fuel. It has a high neutron absorption cross-section (2275 barns). The determination of impurities in uranium and zirconium at the various stages of the nuclear fuel cycle plays an important role in quality control and in the achievement of chemical and metallurgical requirements.

A number of analytical methodologies have been used for the elemental characterization of fuels depending on the target analytes and concentration range of the impurities, required precision, sample throughput, and time of analysis. These methods include inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and graphite furnace atomic absorption spectrometry (GFAAS).

Atomic absorption spectrometry (AAS) is one of the important techniques used in all analytical labora-

ABSTRACT

In the present work, the atomization of Cd in a complex matrix (U+Zr), the matrix effects of the Zr/U+Zr composition, and the matrix concentration of U+Zr are studied. It was found that the matrix composition was finalized to 20%Zr/U+Zr and the total matrix (U+Zr) concentration finalized as 20 mg/mL using graphite furnace atomic absorption spectrometry (GFAAS). The range of analysis was found to be 0.005–0.08 µg/mL for Cd with a 20 mg/mL matrix, resulting in detection limits of 0.005 µg/mL (i.e., 0.25 ppm). The performance of the method was validated by analyzing synthetic samples with a U+Zr matrix. The values obtained for the synthetic samples agreed favorably with the added concentrations. It is of significance to note that the present method gains in importance due to its ability to determine Cd without the need for a prior chemical separation of the U+Zr matrix. The analytical procedure developed could not be applied directly to the analyses of Fast Breeder Reactor sample solutions due to stringent limits. However, matrix separation by the chemical method enables GFAAS analysis to estimate Cd at the required level of 0.1 ppm. The suppression in absorbance in the presence of the matrix was correlated with the atomization mechanism which was based on the activation energy calculation using the Arrhenius plots.

tories working on trace metallic assay of various materials. The strong point in favor of AAS, in particular with an electrothermal atomizer (ETA), is its ability to provide precise results and high sensitivity, and measurements in only a significantly small sample size. In GFAAS, the atomizer suffers physical and chemical interferences, which includes loss of volatile elements like Cd. These types of studies with matrix interference on the Cd signal are performed for beryllium (2) and arsenic samples (3) in our laboratories. However, only a few of our reports have been published from our laboratory on atomic spectroscopic methods for the determination of cadmium in uranium (4-6) and zirconium (7).

Reports are available in the literature for the flame and flameless AAS determination of cadmium in water samples (8-10), high purity iron (11), fish (12), plant (13), tea (14), serum (15), high purity materials (16), milk (17,18), oil (19), blood (20), food (21-23), biological materials (24), environmental samples (25), and soil samples (26,27).

In addition to AAS, other analytical techniques are also in use for the determination of cadmium in food samples by adsorptive stripping voltammetry (28), blood by ICP-MS (29), different environmental water samples with dispersive liquid-liquid microextraction preconcentration combined with ICP-AES (30), and in environmental and biological samples with phase transfer hollow fiber liquid phase microextraction combined with electrothermal vaporization ICP-MS

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(31). Earlier, Huff et al. (32) attempted to determine the trace metal impurities in U-Pu-Zr alloy fuel using anion exchange partition chromatography. While there is a fairly diverse array of data on the behavior of plutonium (33), thorium (34), uranium (4-6), zirconium (7), and the determination of silver in zirconium-uranium matrices (35), no studies of a combined U+Zr system on Cd have been published using the AAS techniques.

The present work focuses mainly on establishing the effect of a U+Zr matrix on the absorbance of Cd. Studies with the change in the analyte absorbance signals and the change in matrix composition %Zr/U+Zr and matrix concentration of U+Zr in GFAAS have helped in the optimization of the method. The suppression was reported with an individual Zr matrix (7) and U matrix (4-6). The absorbance remained more or less constant with a change in %Zr in the U+Zr matrix. A marginal suppression in Cd absorbance was observed in the U+Zr matrix as compared to the pure uranium matrix but a large suppression in Cd absorbance with respect to the matrix-free solution. A comparison of the Cd atom density in pure and in matrix oxides was used to understand the matrix effect on the Cd absorbance signal. These studies were then utilized for the direct determination of Cd at 0.005 µg/mL in the U+Zr matrix with 20%Zr in a 20-mg/mL U+Zr

matrix solution. The range of analysis was found to be 0.005–0.08 µg/mL for Cd with a 20 mg/mL matrix, which leads to detection limits of 0.25 ppm. The performance of the method was evaluated by analyzing synthetic samples of U+Zr.

EXPERIMENTAL

Instrumentation

A computer-controlled GBC-906 atomic absorption spectrometer (GBC Scientific Equipment, Australia), equipped with a GF 3000 graphite furnace atomizer, was used for the determination of Cd. Details of the AAS instrument are reported earlier (35). The atomizer was covered with a shield made of Perspex® which could be removed when access to the atomizer was necessary. Containment of the uranium-zirconium fumes was ensured through an adequate exhaust system provided around the atomizer. The atomizer unit exhaust was connected to a glove box exhaust system (Figure 1).

Standard Solutions

The preparation of U and Zr matrix solutions was reported by our laboratory for uranium (200 mg/mL) and zirconium (14 mg/mL) solutions (35). A cadmium working solution was prepared by appropriate dilution of standard stock solutions (Cd 1 mg/mL in 5% nitric acid; VHG Labs.). To study the

matrix composition effect, a mid-range concentration standard was prepared for Cd with varying amounts of Zr in a U+Zr matrix ranging from 0–40% (zero concentration corresponds to 20 mg/mL U alone). To study the matrix concentration effect, a standard of mid-range concentration was prepared with varying amounts of matrix ranging from 0–40 mg/mL. After optimizing the matrix proportion, a series of standard solutions was prepared with and without matrix [4 mg/mL Zr, 16 mg/mL U, and 20 mg/mL 20%Zr+U (4 mg/mL Zr + 16 mg/mL U)] matrix and graded concentrations of Cd in the range of 0–100 ng/mL. In the absence of certified reference materials with this matrix, three synthetic samples of (U+Zr) were prepared with a matrix of 20 mg/mL 20%Zr+U (i.e., 4 mg/mL Zr + 16 mg/mL U) and graded concentrations of Cd at 0.016, 0.03, and 0.05 µg/mL which is equivalent to 0.8, 1.5, and 2.5 ppm (µg/g) in a 20 mg/mL Zr+U matrix.

Instrumental Parameters

The instrumental parameters used for Cd are given in Table I. Argon gas of purity 99.995 vol. % was used as a purge gas.

The fundamental conditions of GFAAS analysis (such as temperature and time durations at pre-atomization and atomization steps) were investigated in order to identify the

Fig. 1. Schematic of atomizer with glove box exhaust system.

optimum conditions for obtaining stable and sensitive atomic absorbance signals for Cd with and without matrix. The detailed procedure adopted here was similar to that followed earlier for trace metal analysis of Cd in a BeO matrix (2). A Model M/s Raytek® two-color optical pyrometer (Raytek, USA), sensitive in the range of 1000–3000 °C, was used to measure the temperatures in the atomization stage. Cd absorbance was monitored as a function of (a) matrix composition on a fixed concentration of Cd and varying zirconium proportions in the range 0–40% Zr and (b) matrix concentration in the range 0–40 mg/mL of U+Zr using fixed analyte concentrations. The characteristic concentration was obtained for Cd by analyzing three sets of standards, i.e., one each in 4 mg/mL Zr, 16 mg/mL U, 20 mg/mL U+20%Zr, and without matrix with a graded proportion of Cd.

The study on the atomization of Cd in a matrix-free solution as well as in a U+Zr matrix has resulted in the optimization of the analytical procedure for the analysis of the Cd/U+Zr matrix.

The atomization mechanism for Cd atomization was studied using the absorbance-time-temperature profile of the absorbance signal. From the initial portion of the profile at various temperature points, corresponding absorbance signals were measured. From these data

TABLE I
Instrumental Parameters
for Cd With GF-3000 AAS

Wavelength	228.1 nm
Spectral Bandwidth	0.5 nm
Lamp Fill Gas	Ne
Lamp Current	5 mA
Gas Used	Ar
Flow Rate ^a	6 L/min

^a Only during 'dry' and 'pre-atomization' stage.

points, the Arrhenius plot of log absorbance vs. inverse of absolute temperature was obtained and used to calculate the activation energies (E_a); signal appearance temperatures (T_{app}) were obtained from the absorbance profile for matrix and matrix-free solutions. The appearance temperature is the temperature producing a just noticeable signal above the blank absorbance.

Separation of Major Matrix

To utilize the separated samples from the matrix for the determination of Cd, a mid-range concentration at 0.04 µg/mL standard was prepared for Cd in a 20%Zr/U+Zr matrix at 1 g/mL solution. For quantitative chemical separation of the analytes, 30%TBP/dodecane in 7M HNO₃ was used. To utilize the separated method for the determination of the analyte, it is important to understand the effect of U+Zr in raffinate solution on the Cd absorbance. Therefore, to study the matrix effect in a raffinate solution, a Cd (0.04 µg/mL) standard was prepared with varying amounts each of 20%Zr/U+Zr matrix at much lower matrix concentrations (in the range 10–50 µg/mL).

RESULTS AND DISCUSSION

In GFAAS, atomization of an analyte in the presence of a complex matrix such as Pu, U, Zr, and Th is the result of an interaction of analyte matrix, analyte-carbon, or carbon matrix (34). Earlier we carried out investigations in matrices such as U (5), Th (36), Zr (7), and U+Pu (37) on the absorbance and atomization behavior of Cd. Inference drawn from these studies shows that the absorbance of Cd is found to be different in the matrix compared to a matrix-free solution. These results propelled us to investigate similar studies in U+Zr, a fuel proposed for fast breeder reactors. The atomization behavior of Cd was, therefore, studied to under-

stand the effect of Zr, U, and U+Zr by measuring the atomic absorption signal for Cd with and without a matrix.

The experimental parameters such as pre-atomization and atomization temperatures were optimized for Cd in matrix-free solutions. The effect of pre-atomization was investigated on the absorbance of Cd in the temperature range of 200 to 500 °C. The temperature is critical in the case of Cd because Cd(NO₃)₂ decomposes at 334 °C to oxide (CdO), which boils at T_{bo} =765 °C and hence, the possibility of pre-atomization losses are high for the analyte at high temperatures (38). The optimized temperature was 300 °C for pre-atomization of the analyte. Studies on the atomization behavior in the temperature range of 1900 to 2700 °C showed that the optimum temperature for atomization was 2300 °C. A similar optimization studied in the presence of a uranium matrix was found to be 500 and 2300 °C for pre-atomization and atomization, respectively.

Effect of Matrix Composition

Using the optimized uranium matrix parameters, the effect of matrix composition was studied by varying the Zr percentage in the U+Zr matrix from 0–40%, keeping the total matrix concentration as 20 mg/mL at 0.04 µg/mL of Cd. The results indicated that the Cd absorbance signal remained unaffected in the range of 0–40% Zr in the (U+Zr) mixed matrix with 20 mg/mL total matrix. As can be seen from Table II, the absorbance remains essentially the same irrespective of the data collected from 0–40% or 40–0% Zr on a new graphite atomizer each time, unlike Ag in the U+Zr matrix (35).

This probably can be explained on the basis of the effect of uranium and zirconium matrices on Cd and Ag absorbance. In the pres-

ence of 20 mg/mL of U matrix, the Cd (5) and Ag (39) absorbance of both analytes is suppressed enormously, while at 10 mg/mL Zr matrix the Cd absorbance suppressed to 50% (7) and did not change the absorbance of Ag (40). The presence of a combined matrix (U+Zr) did not change the absorbance of Cd with a change of Zr at 0–40% concentration in the U+Zr matrix. It also remained the same when the Zr content is changed from 40–0%/U+Zr matrix. This means that the Cd absorbance remained the same every time when studies were carried out with a 0–40% or 40–0%Zr/U+Zr matrix on a new atomizer. However, the presence of the Zr matrix does not show any suppression for Ag (40) and hence, studies in which the percentage of Zr was increased and decreased were found to be affected differently.

Effect of Matrix Concentration

A study on the atomization of Cd in a mixed matrix was carried out with varying concentrations of the matrix (0–40 mg/mL). The variation obtained in absorbance signal as a function of matrix concentration is shown in Figure 2. As can be seen from the data, a suppression in the absorbance signal was observed with an increase in matrix concentration up to 40 mg/mL. With an increase in concentration, the variation in Cd absorbance is not much (from 5–20 mg/mL) and a higher matrix concentration is always pre-

ferred as it provides better detection limits. Therefore, for further studies, a 20 mg/mL concentration was used.

Zr, U, and U+Zr Matrix Effect

20 mg/mL of 20%Zr in U+Zr matrix contains 16 mg/mL U and 4 mg/mL Zr. So, the effect of individual matrixes was also studied. It was observed that in the presence of 16 mg/mL U matrix, the absorbance signal for Cd was reduced to ~40% in comparison to that observed in matrix-free solution. It was observed that in the presence of 4 mg/mL Zr matrix, the absorbance signal for Cd was reduced to ~50% in comparison to that observed in a matrix-free solution.

To understand the suppression of Cd absorbance in the presence of the matrix, the reaction mechanism involved in the atomization of Cd in the presence and absence of the matrix was studied using the Arrhenius plots of $\ln(A)$ vs. T^{-1} .

The studies so far reported in the literature are all carried out on analytes with water or weak acids (41). The nature of the reaction mechanism gets significantly altered when atomization of the analytes in the presence of complex matrices such as U and U+Zr takes place. The present data deals with the study of the reaction

mechanism involved in the atomization of Cd from U and U+ Zr matrixes. Activation energy (E_a) values were calculated from the Arrhenius plot in a similar manner as reported earlier (41). The plot of log absorbance as a function of inverse of the absolute temperature should yield one or more straight lines with slope = $-E_a/2.303 R$, where R represents the gas constant.

Since construction of a log absorbance versus $1/T$ plot requires that the temperature of the atomic vapor be equal to that of the surface of the furnace, absorbance measurements for E_a value calculations were restricted to the initial few hundred milliseconds of the absorption profile (see Figure 3, Absorbance - Time profile). Absorbance data taken from this region of the curve were used to construct the E_a plots.

The E_a plots were obtained in the presence of matrices for Cd. Signals T_{app} and E_a were found to be the same in both the aqueous and (U, Zr) matrix, i.e., independent of the matrix. The values are listed in Table III.

To support our findings of the E_a value, the thermodynamic data were taken from the literature (41) for comparison. The dissociation energy values obtained in our studies were 294 kJ/mol and 315 kJ/mol

TABLE II
Absorbance Signal With Zr/Zr+U Ratio Decreasing
and Absorbance Signal With Zr/Zr+U Ratio Increasing

Zr% Decreasing on 0.08 µg/mL Cd			Zr% Increasing on 0.08 µg/mL Cd		
%Zr	%U	Absorbance	%Zr	%U	Absorbance
40	60	0.286	0	100	0.224
20	80	0.282	5	95	0.211
10	90	0.292	10	90	0.255
5	95	0.248	20	80	0.301
0	100	0.274	40	60	0.301

Fig. 2. Matrix concentration; effect on 0.08 µg/mL Cd.

for cadmium oxide in a matrix-free and U+Zr matrix, respectively, and these are rather close to correspondingly reported (41) values ($\text{CdO} = 340 \text{ kJ/mol}$). In the present studies, therefore, it was concluded that dissociation of the oxide is the only mode of atomization for Cd. From the E_a energy values, we can infer that most probably the species available prior to T_{app} are CdO(s) and therefore the sequence of atomization suggested is as follows:

Having obtained a value of E_a and a possible atomization sequence, it is necessary to ensure that the resulting intermediate satisfies physical constants. Here, from the E_a data, the oxide in solid state was the precursor to the gaseous atoms. At T_{app} the CdO(s) was in solid state (melting point - $\text{CdO(s)} = 1173^\circ\text{C}$) and once dissociated, Cd goes to gaseous form directly (boiling point - $\text{Cd} = 334^\circ\text{C}$).

The mode of atomization and possible intermediate reactions are useful in understanding the possible interference effects in case of complex matrices. It was observed that the slope of the calibration curves obtained for the aqueous medium was significantly altered when uranium, zirconium, and U+Zr matrices were introduced, suggesting strong matrix influence on the atomization behavior of Cd.

Fig. 3. Typical absorbance-time profile showing the part of the curve from which the data were taken.

Since signal appearance temperatures and E_a values remained the same in the aqueous, Zr, U, and U+Zr matrices, suppression of the absorbance in the presence of Zr, U, and U+Zr matrices could not be explained from these studies.

GFAAS provides only indirect information of the atomization process of the analytes occurring in a graphite atomizer. We tried to explain the change in analyte atomization efficiency in the presence of the matrix with the dissociation of the analyte nitrates, uranyl nitrate/uranium+zirconium nitrate. Thermogravimetric analysis (42) shows the decomposition of uranyl nitrate to its dioxide in the temperature range of $297\text{--}1297^\circ\text{C}$ and zirconium nitrate as follows:

Both uranium, zirconium, and U+Zr nitrates get converted into their respective dioxides. Both UO_2 and ZrO_2 thus formed are very stable lattices. Similarly, the Cd also gets converted into the oxide, mostly dissolved in the main lattice of UO_2 and (U+Zr) O_2 . The diffusion rates of the cationic elements in these lattices are very low (33). A small amount of the analyte dissolved in the (U,Zr) O_2 lattice con-

siderably reduces the chemical activities, hence the detectability and suppression in absorbance in the presence of the matrix. UO_2 and ZrO_2 dissociate only above 3000°C , which is not attainable in the GF atomizer. Hence, the analytes remain trapped in the $\text{UO}_2\text{+ZrO}_2$ lattice, which explains the poor atomization efficiency.

Having finalized the percentage of Zr and the concentration of the matrix, the experimental parameters were again optimized with 20%Zr/U+Zr at 20 mg/mL matrix. For optimization of the GFAAS measurement parameters, the effects of the pre-atomization and atomization temperature on the Cd absorbance were freshly investigated on the GF 3000. The results of the pre-atomization/atomization studies for uranium are shown in Table IV.

The optimized temperatures for pre- and atomization are finalized at 400 and 2300°C , respectively. The optimized experimental parameters with $5 \mu\text{L}$ /loading of 20%Zr/U+Zr at 20 mg/mL concentration are shown in Table V.

Successive loadings of (U+Zr) solution leads to matrix buildup inside the graphite atomizer. However, this buildup of matrix did not have any significant effect on the Cd ($0.04 \mu\text{g/mL}$) absorbance with repetitive loading of the 20.0 mg/mL mixed matrix on the same atomizer. The absorbance remained constant with repetitive loading of the sample for 80 atomization cycles.

TABLE III
Activation Energies of the Atom Formation for Cd
(in aqueous and U+Zr)

Element	Applied Temp. ($^\circ\text{C}$)				Activation Energy (kJ/mol)		
	Aqueous		U+Zr		Obtained	Reported	
	Obtained	Reported	Obtained	Reported	Aqueous	U+Zr	Aqueous
Cd	500	447	500	-	294 ± 29.4	315 ± 31.5	340

Using freshly optimized parameters with the U+Zr solution, a method was developed for the direct determination of Cd in a 20 mg/mL of U+20%Zr matrix using the 2288 nm spectral line. Measurements of the atomic absorption signals for Cd were carried out over a wide range of concentrations using standard solutions in these matrices. The linear analytical ranges in the presence and absence of the matrices were obtained. The analytical data on the Cd absorbance in aqueous, 4 mg/mL Zr, 16 mg/mL U, and 20 mg/mL (20%Zr/U+Zr) matrices are shown in Figure 4.

Characteristic concentrations (C.C.), the smallest amount determined and range of the analysis in the presence and absence of the

matrix, are given in Table VI. The working linear analytical curves for 4 mg/mL Zr, 16 mg/mL U, and 20 mg/mL (20%Zr/U+Zr), along with a matrix-free solution, are also shown in the table. As can be seen, the analytical range and sensitivity of the methodology is poorer in a matrix relative to a matrix-free solution.

Peak profiles were plotted at 0.04 $\mu\text{g/mL}$ Cd in the absence and presence of different matrices (4 mg Zr/mL, 16 mg U/mL, and 20 mg/mL 20%Zr+U) (Figure 5). The area, time to reach peak, and width of the different matrices were calculated from the curves and are shown in Table VII. It was observed that the peak profile broadened; peak area reduced in

the presence of the matrices as compared to the matrix-free solutions. An increase in peak width can be attributed to a slow analyte release. This indicates that the matrix plays a major role in signal suppression. The stable lattice and closed packed face-centered cubic structure of urania and zirconia acts as an entrapment for the Cd atoms, resulting in the suppression of the Cd absorbance signal in the matrix.

The performance of the above method was evaluated by analyzing synthetic samples containing Cd in 20%Zr+80%U. Using the standardized procedure, three synthetic samples were analyzed. The results obtained from the analysis of these synthetic samples are shown in Table VIII. A comparison of these

Fig. 4. Analytical curves for Cd in aqueous, 4 mg/mL Zr, 16 mg/mL U, and 20 mg/mL (20%Zr/U+Zr) matrices.

Fig. 5. Peak profiles for Cd in aqueous, U, Zr, and U+Zr matrices.

TABLE IV
Optimization of Experimental Parameters for Cd at 0.08 $\mu\text{g/mL}$ in U+Zr Matrix With 20% Zr

Pre-atomization Temperature for 30 s			Atomization Temperature at 0.3 s		
Temp. (°C)	Matrix Blank	Cd Signal	Temp. (°C)	Matrix Blank	Cd Signal
300	0.008	0.238	2100	0.008	0.193
400	0.002	0.246	2200	0.002	0.227
500	0.002	0.251	2300	0.002	0.261
600	0.002	0.256	2400	0.004	0.260
700	0.004	0.230	2500	0.004	0.244

TABLE V
Optimized Experimental Parameters of GF for Cd in U+Zr

Atomizer Stage	Temp. (°C)	Time (s)	
		Ramp	Hold
Dry	80	5	10
	120	10	10
	300	5	10
Pre-atomize	500	0.2	10
Atomize	2300	0.9	0.3
Cooling	20	14.5	10.0

results based on 8–10 replicate measurements indicates close agreement for all determinations. The replicate analyses of the synthetic samples resulted in the precision of the method to be better than 8% RSD.

The influence of mixed matrices on the Cd atomization behavior showed that the Cd sensitivity is poorer in mixed matrices as compared to pure nitrate solutions, but did not change with a change in percentage of Zr. It is, therefore, necessary to match the standard and sample compositions in the mixed matrix. The matrix composition was finalized to 20%Zr/(U+Zr) for further studies. The range of analysis was found to be 0.005–0.08 µg/mL for Cd with a 20 mg/mL matrix, which results in detection limits of 0.25 ppm.

It is possible to determine Cd in a Zr+U matrix successfully using the optimized methods. In view of the high detection limits obtained for the analyte in a uranium-zirconium matrix, the method is not

meeting the specification limits required for the analyte in FBR fuels. The poor atomization efficiency in the presence of U+Zr is correlated with the entrapment of the analytes in the stable lattices of urania and zirconia in addition to a release of oxygen in a uranium matrix. Further studies were, therefore, conducted from uranium + zirconium separated and pre-concentrated solutions using GFAAS.

Separation Procedure

The specification limit for Cd in Zr+U is at 0.1 ppm level. To achieve the desired low detection limits at the 0.1 ppm level for Cd, an alternate method was developed which involved chemical separation of the matrix and analysis of the raffinate using GFAAS. Chemical separation procedures based on solvent extraction/ion exchange can be used for this purpose; however, the former procedure, being faster, is preferred. Since quantitative chemical separation of the analyte is most essential, detailed studies were carried out to select

proper extractants, diluent, and aqueous medium which would facilitate the same. Solvent extraction procedures have been developed using different extractants for the analysis of common metals in U+Zr bearing fuel samples (43) and in U-Pu-Zr (32). However, in the present studies, the methods used are 30%TBP/CCl₄ in 7M HNO₃ (44) for the separation of the matrix and for analysis. It was reported (44) that with 30%TBP+70%CCl₄ in 7M HNO₃, a selective simultaneous extraction of U and Zr into the organic phase can be achieved. In the present studies, the same extraction procedure was applied using 100 mg U+Zr. The effect of U+Zr in the raffinate on Cd was also estimated.

It was reported (44) that during separation of 1 g Zr+U, the raffinate contains analytes and a small amount of matrix. The matrix concentration in the raffinate was in the range of ~10–50 µg/mL. Therefore, to utilize the separated method for the determination of

TABLE VI
Characteristic Concentrations (C.C.), the Smallest Amount Determined and Range of Analysis

Matrix	C. C. (ng/mL)	Linear Analytical Range		LOQ (g)	
		(µg/mL)	(ppm) (µg/g)	Present	Reported (37)
Aqueous	0.2	0.002–0.08	-	1.0x10 ⁻¹¹	0.5x10 ⁻¹²
4 mg/mL Zr	0.25	0.005–0.08	1.25–20.0 ^a	2.0x10 ⁻¹¹	-
16 mg/mL U	0.35	0.005–0.08	0.3125–5.0 ^b	2.0x10 ⁻¹¹	-
20 mg/mL U+Zr	0.3	0.005–0.08	0.25–4.0 ^c	2.0x10 ⁻¹¹	-

^a Based on 20 µg of Zr, ^b Based on 80 µg of U, ^c Based on 100 µg (Zr/U+Zr) in 5 µL of solution.

TABLE VII
Calculated Profiles of Area of Different Matrices, Time to Reach Peak, Width, and Height

Sample	Matrix	Area	Peak at (ms)	Width
1	Matrix-free	89.35	350	375
2	16 mg/mL U	81.65	400	521
3	20 mg/mL U+Zr	69.45	425	475
4	4 mg/mL Zr	67.125	375	525

TABLE VIII
Results of Analysis of Three Synthetically Prepared Samples for the Determination of Cd at ppm

Sample	Concentration of Spike (ppm)		RSD (%)
	Added	Obtained	
1	0.8	0.77	0.775
2	1.5	1.51	1.45
3	2.5	2.34	2.35

Cd, it is important to understand the effect of 10–50 µg/mL Zr+U in the raffinate on Cd. The effect of 20%Zr/Zr+U on Cd was also studied at the concentration of 0.04 µg/mL. It was observed that the Cd absorbance remained unaffected with an increase in matrix concentration in the range of 10–50 µg/mL. In order to achieve the desired detection limit of 0.1 ppm for the element, a method was developed using U+Zr samples after chemical separation with 30%TBP/dodecane in 7M HNO₃. Four times the chemical separation was applied using 30%TBP/dodecane in 7M HNO₃ for the near total removal of the matrix. The detection limits obtained with this method were 0.1 ppm for Cd.

The results of the aqueous samples obtained with the GBC-906 GFAAS were also validated using the SPECTRO ARCOS SOP ICP-AES independently. However, ICP-AES suffers from severe spectral interference in the presence of Zr (44) and U (45) matrices with line-rich emission spectra and hence, the samples were analyzed only in aqueous solutions. However, it was found that the Cd estimations by ICP-AES were not affected in the presence of 10–50 µg/mL U+Zr as well. The results of the analysis of the synthetic samples with varying concentrations of matrix and a real sample analyzed using the GBC-906 GFAAS and SPECTRO ARCOS SOP ICP-AES are shown in Table IX.

CONCLUSION

These studies showed that the Cd absorbance signal kept decreasing with an increase in matrix concentration ranging from 0–40 mg/mL of U+Zr. Attempts were made to understand the effect of Zr+U on analyte absorbance and the reaction involved in the atomization of the analyte in the matrix. The matrix concentration was optimized to 20 mg/mL. To use the

TABLE IX
Analysis of Synthetic Samples With Varying Concentrations of Matrix and a Real Sample Obtained With the GBC-906 GFAAS and SPECTRO ARCOS SOP ICP-AES

Sample No.	Expected Cd	Concentration of Spike (µg/mL)			
		GFAAS		ICP-AES	
		Obtained	(%) RSD	Obtained	(%) RSD
1.	0.05 matrix-free	0.05	5	0.051	<5
2.	0.05+10 µg/mL matrix	0.054	7	0.055	<5
3.	0.05+20 µg/mL matrix	0.049	6	0.056	<5
4.	0.05+50 µg/mL matrix	0.05	5	0.06	<5
5.	0.05 real sample	0.054	5	0.056	<5
6.	0.1 matrix-free	0.1	5	0.1	<5
7.	0.1+10 µg/mL	0.11	7	0.107	<5
8.	0.1+20 µg/mL matrix	0.105	6	0.106	<5
9.	0.1+50 µg/mL matrix	0.098	5	0.11	<5
10.	0.1 real sample	0.1	5	0.11	<5

method for uranium-zirconium mixed oxide samples, the effects of varying concentrations of Zr in a Zr+U mixed matrix were studied. The results indicated that the absorbance signal remained unaffected in the range of 0–40% Zr in a (Zr+U) mixed matrix with 20 mg/mL total matrix. Cd can be determined by GFAAS in 20%Zr/Zr+U samples in the range of 0.005–0.08 µg/mL, which leads to 0.25 ppm on a 20 mg/mL sample basis. Though the method is not suitable to determine Cd directly in fast breeder reactor (FBR) fuels due to stringent specification limits, matrix separation by the chemical method enables GFAAS to estimate Cd at the required level of 0.1 ppm using the raffinate containing a matrix of 50 µg/mL of matrix.

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