Development of Analytical Methods for the Direct Determination of Silver in Plutonium-Thorium and Uranium-Thorium-Based Fuels Using GFAAS

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ABSTRACT

Studies on the atomization of silver in Pu+Th and U+Th matrices were carried out. The effect of matrix composition and its concentration on Ag absorbance using graphite furnace atomic absorption spectrometry (GFAAS) was investigated. These studies showed that the absorbance signal observed for Ag in a mixed matrix was enhanced compared to that observed for a pure thorium matrix, but it is poorer than in matrix-free solutions. The enhancement was found to be more pronounced in a Pu+Th than in U+Th matrix. The difference in the behaviors of Ag atomization efficiency in these matrices is explained on the basis of change of pO_2 during dissociation of plutonium nitrate and uranyl nitrate at the atomization temperature of silver. Accumulation of Pu and U with successive loading in the graphite atomizer did not have any additional effect on the ana-

lyte absorbance. Based on these investigations, two analytical methods using GFAAS were developed for the direct determination of Ag in the 0.1–4.0 ppm range on the basis of 20 mg/mL each of (Pu+Th) and (U+Th) solution with 3% Pu and 3% U, respectively.

The performance of these methods was evaluated by analyzing synthetic samples of Pu+Th and U+Th. The values obtained for 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 silver without the need for a prior chemical separation of the Pu+Th and U+Th matrices. The analytical procedure developed could be applied for the rapid analyses of Advance Heavy Water Reactor (AHWR) sample solutions without pre-treatment of the samples such as separation and pre-concentration of the matrix.

of low-density pyrocarbon, high-density pyrocarbon, silicon carbide and high-density pyrocarbon, with silicon carbide being the main barrier for the metallic species. These so-called TRISO fuel particles retain quite effectively most of the important fission products like cesium, iodine, xenon, and krypton up to temperatures of 1000 °C, but the release of silver seems to present a major problem. Despite the low fission yield of the stable ^{109}Ag (0.03% for ^{235}U) and its low conversion rate of 0.1% to $^{110\text{m}}\text{Ag}$ by neutron capture, the latter is considered as one of the key fission products. Total Ag concentration, therefore, should be monitored in AHWR fuel since its isotope $^{110\text{m}}\text{Ag}$, with a relatively long half-life of 253 days, has a high γ -ray dose rate (2).

The determination of silver in the presence of various nuclear materials such as 25%Pu in (Pu-U) (3), U (4), Th (5) were reported earlier from our laboratory. However, the application of GFAAS for determining Ag has not been investigated in the presence of Pu+Th and U+Th matrices. Reports are also available for silver determination in wine (6), urine (7), geological and related materials (8-9), teeth (10), precious metals (11), blood (12), steel (13), environmental samples (14), and water samples (15) by flame and flameless AAS.

In addition to AAS, other analytical techniques are also in use to determine silver in polymeric samples by absorption, mass and X-ray spectrometry (16); seawater (17) by sensitive sector field inductively coupled plasma mass spectrometry (SF-ICP-MS); edible oils by inductively coupled plasma optical emis-

INTRODUCTION

Due to the increasing availability of ^{239}Pu as a by product of spent U-bearing nuclear fuels and also due to the attractive fissile behavior of ^{239}Pu , plutonium-bearing nuclear fuel materials are becoming promising substitutes to ^{235}U -enriched fuels in thermal and fast reactors. The strict quality control on the purity of these materials has to be assured during the fuel fabrication

process. The Advance Heavy Water Reactor (AHWR), therefore, was proposed to have ^{235}U , ^{233}U , and ^{239}Pu . The AHWR (1) was conceived to use fuel comprised of solid solutions of plutonium-thorium and uranium-thorium in the form of their oxides. Of these, plutonium-thorium fuel shall have 2.5% and 4% Pu and uranium-thorium fuel shall contain 3% and 3.75% of uranium in AHWR.

Recent Compact High Temperature Reactor (CHTR) designs generally make use of fuel kernels surrounded by four successive layers

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sion spectrometry (ICP-OES) (18); and milk by ICP-MS (19). The determination of Ag in (Pu+Th) and (U+Th) matrices has not yet been reported in the literature.

The present study examines the change in the analyte absorbance signals with a change in matrix composition of %Pu/Pu+Th and %U/U+Th and the concentration of Pu+Th and U+Th using GFAAS analysis. These studies were then utilized for the direct determination of ppm amounts of silver in Pu+Th and U+Th matrix with 3% Pu and 3% U, respectively, employing GFAAS. The mechanism of release of gaseous atoms from the solid lattice in GFAAS has previously been investigated by thermodynamics-kinetics approaches (20). It was noted that though the nitrate solution of either Ag or Pu+Th/U+Th was loaded, nitrates get converted to oxides of Ag, Pu+Th and U+Th. Ag has to be released from the Pu+Th and U+Th oxide lattices.

A comparison of the analyte atom density in pure and in matrix oxides was used to understand the matrix effect on the Ag absorbance signal. An enhancement was observed in the (Pu+Th)/(U+Th) matrix as compared to a pure thorium matrix. The enhancement was found to be more pronounced in the Pu+Th than in the U+Th matrix and this was correlated with the release of oxygen during dissociation of the matrices (3).

EXPERIMENTAL

The two different instruments were used for the determination of Ag in the Pu+Th and U+Th matrices:

Instrumentation

To analyze Pu-bearing samples, a Varian Techtron Model AA-6 atomic absorption spectrometer (Varian Techtron, Australia), equipped with a carbon rod atomizer (CRA-63, Mini Massmann) and BC-6 background corrector, operating in peak

height measurement mode, was used. The AAS unit was adapted for radioactive work by modifying the modular setup by placing the isolated atomizer in a glove box environment and details have been given earlier (21).

To analyze U and Th samples, a computer-controlled GBC-906 atomic absorption spectrometer, equipped with a GF 3000 graphite furnace atomizer and programmable sample dispenser, was used for the determination of Ag (GBC Scientific Equipment Pty., Ltd., Australia). The graphite furnace was pyrolytically coated and atomization was secured from the sample loaded inside the graphite atomizer. The atomizer was covered with a shield made of Perspex® which can be displaced when access to the atomizer was necessary. Containment of uranium-thorium fumes was ensured through the adequate exhaust system provided around the atomizer. The atomizer unit exhaust was connected to a glove box exhaust system and was described earlier in detail (22). Our laboratory previously reported the details of the preparation of plutonium (40 mg/mL) (23), uranium (40 mg/mL), and thorium (200 mg/mL) solutions (24) along with the procedure adopted.

Silver working solutions were prepared by appropriate dilution of the standard stock solutions (1 mg/mL Ag in 5% nitric acid, (VHG Labs, Manchester, NH, USA).

The instrumental parameters for Ag, using both of the instruments, are given in Table I.

Argon gas of 99.995% purity was used as the purge gas.

To study the matrix effect, a standard of mid-range concentration was prepared for Ag with varying amounts each of Pu+Th and U+Th matrix ranging from 0–40 mg/mL (zero concentration corresponding to 0 mg/mL Th).

To study the effect of varying amounts each of plutonium and uranium in the Pu+Th and U+Th matrices, mid-range concentration standards were prepared for Ag with Pu and U ranging from 0–10%, with an overall matrix concentration fixed at 20 mg/mL. After optimizing the matrix portion for direct determination of Ag in the Pu+Th and U+Th matrices, a series of standard solutions were prepared each containing 20 mg/mL 3%Pu/Pu+Th (0.6 mg Pu/mL + 19.4 mg Th/mL) and 3%U/U+Th (0.6 mg U/mL + 19.4 mg Th /mL) and graded concentrations of Ag in the range of 0–100 ng/mL from the Ag stock solution.

In the absence of certified reference materials with these types of matrices, three synthetic samples of (Pu+Th) and (U+Th) were prepared similarly. These were used as reference samples for obtaining precision and to validate the method developed here.

The fundamental conditions of GFAAS analysis (such as temperature and time durations at the pre-atomization and atomization steps) were investigated in order to identify the optimum conditions for obtaining stable and sensitive atomic absorbance signals for Ag in Pu+Th and U+Th as well as in the matrix-free solution. The detailed procedure adopted here was similar to that followed earlier for trace metal analysis of Ag in plutonium-uranium (3), and for 3%Pu+Th and in uranium-thorium for 3% U+Th

TABLE I
Instrumental Parameters for Ag with CRA-63 and GF-3000 AAS

Wavelength	328.1 nm
Spectral Bandwidth	0.5 nm
Lamp Fill Gas	Ne
Lamp Current	5 mA
Gas Used	Ar
Flow rate	6 L/min

(24). Ag absorbance was monitored as a function of (a) matrix concentration in the range 0–40 mg/mL each of Pu+Th and U+Th using fixed analyte concentrations; (b) matrix composition on a fixed concentration of Ag and varying plutonium/uranium proportions in the range 0–10% Pu and U. Characteristic concentration was obtained for Ag by analyzing two sets of standards, i.e., one each in 3% Pu+Th and 3% U+Th with graded portions of Ag.

RESULTS AND DISCUSSION

In GFAAS, atomization of an analyte in the presence of a complex matrix (such as Pu, U, and Th) is the result of an interaction of analyte-matrix, analyte-carbon, or carbon-matrix. It was reported that the atomization behavior of silver changed in the presence of Pu/U/Th matrices (3–5). It was also reported that the absorbance signals for Ag was reduced significantly in uranium (4) and thorium (5) compared to that observed in aqueous solution, while the absorbance signal showed an enhancement when plutonium was added to the uranium solution (3). These studies led us to investigate the effect of matrix concentration as well as matrix composition on analyte absorbance for the mixed matrix of Pu+Th and U+Th solutions.

An investigation of the GFAAS measurement parameters (pre-atomization temperature, atomization temperature, and time) is very important for achieving precise and sensitive atomic absorbance measurements. The pre-atomization temperature is critical in the case of silver since AgNO_3 dissociates to silver oxide (Ag_2O) at 300 °C, which decomposes immediately, and Ag atomization takes place at 877 °C (25). For optimization of the GFAAS measurement parameters, effects of the pre-atomization and atomization temperature on the absorbance were investigated on GF 3000 in the temperature range of 300–700 °C for Ag in 20 mg/mL thorium matrix. As seen from Table II, the S/N ratio was maximum at 600 °C. The effect of the atomization temperature on the absorbance of Ag was similarly investigated over a temperature range 2100 to 2500 °C. A constant and maximum absorbance was obtained at an atomization temperature of 2300 to 2400 °C. Based on these observations, pre-atomization and atomization temperatures and time durations were selected for Ag using the proposed procedures which were 600 °C/30 s and 2300 °C/0.3 s, respectively. The results of the pre-atomization/atomization studies for thorium are listed in Table II.

Effect of Matrix Composition

The effect of matrix composition was studied by varying the plutonium/uranium percentage in the thorium matrix from 0–10%, keeping the total matrix concentration as 20.0 mg/mL at 0.04 µg/mL Ag. It was observed that with an increase in plutonium composition in the Pu+Th matrix, Ag absorbance increased by 15% with 2% Pu as compared to the pure Th solution (0% Pu); then it remained unaffected with an increase in Pu at 2–4% concentration in the Pu+Th matrix. The effect of uranium in the thorium matrix was seen on Ag absorbance by varying the U concentration from 0–10%, keeping the total matrix concentration as 20 mg/mL. It was observed that with an increase in uranium concentration up to 2% in the U+Th matrix, the Ag absorbance increased by 12% as compared with Th alone, and then onwards remained unaffected in the range of 2–4% U. The expected percentage of Pu/U in AHWR fuel is 2–4%. Hence, in further studies, the Pu/U composition was kept at 3%Pu/3%U in the mixed matrix. However, beyond 4 to 10%, the rise was insignificant for both of the mixed matrices. The results are shown in Table III.

TABLE II
Optimized Experimental Parameters
for Ag at 0.04 µg/mL in Th

Pre-atomization Step Temperature at 2300 °C			Atomization Step Temperature at 600 °C		
Temp. (°C)	Matrix	Absorbance	Temp. (°C)	Matrix	Absorbance
300	0.008	0.238	2100	0.008	0.193
400	0.002	0.256	2200	0.002	0.227
500	0.002	0.260	2300	0.002	0.281
600	0.002	0.281	2400	0.004	0.280
700	0.004	0.230	2500	0.004	0.265

TABLE III
Effect of Increase of %Pu and %U
on Ag Absorbance in Mixed Matrices

20 mg/mL Matrix With Varying Composition of %Pu/U	Absorbance	
	Ag/Pu+Th 0.04 µg/mL	Ag/U+Th 0.04 µg/mL
Aqu. (matrix-free)	0.74	0.74
0	0.314	0.314
2	0.370	0.350
3	0.370	0.355
4	0.370	0.354
5	0.363	0.360
10	0.370	0.364

Our laboratory reported earlier (24) that with a progressive increase in %U/U+Th matrix, the Mg absorbance is suppressed; while in present studies, Ag absorbance enhanced with the addition of uranium in a thorium matrix. This can be explained on the basis of uranium and thorium chemistry. With thorium, the matrix-carbon interaction competes with the analyte-carbon interaction since thorium has a higher carbon affinity and preferentially forms a uniform stable ThC₂ layer. Unlike in the case of Mg (24) in U+Th, wherein 0.1 mg/mL matrix was used, i.e., 0.097 mg/mL Th. Carbon of the graphite tube was not fully utilized with each loading of the (U+Th) matrix. Thorium, due to repeated loading of the mixed (U+Th) matrix, was all used to keep making the stable ThC₂ layer; and the UO₂(NO₃)₄ of the mixed matrix was free and forms carbide through oxide. The UC/UC₂ remained on the surface. It dissolves with 0.1 M HNO₃ from loading of the next aliquot and forms uranyl nitrate again. Hircq (27) reported the re-dissolution of UC/UC₂ from the next loading of the nitrate solution in the atomizer using the following equation:

This uranyl nitrate on dissociation gives free [O] and in turn suppresses Mg absorbance (24). Thermo-gravimetric (26) studies on ThO₂ - 2% U₃O₈ granules also showed a continuous decrease in weight in the temperature range of 400-1500 °C. The weight loss was mainly attributed to a release of oxygen from U₃O₈. Dissolution of thoria essentially requires HF along with HNO₃. Hence, it did not dissolve in HNO₃ during the next aliquot loading.

In the present studies, 200 times more matrix was loaded every time in comparison to the Mg (24) determination. A uniform stable ThC₂ layer is formed during the initial stage itself in the atomizer due to the availability of more thorium, and Pu/U is trapped in the stable lattice of ThC₂. The thoria lattice is very stable and has a defect-free structure due to its stoichiometric composition. The presence of U/Pu atoms leads to lattice defects in thoria. The presence of these lattice defects assists faster diffusion (28) of silver in Pu+Th and U+Th oxides compared to the thorium carbide/oxide layer. These changes increased the mobility of the Ag atoms and showed an increase in Ag

absorbance in the presence of Pu/U compared to thorium matrix alone.

Effect of Matrix Concentration

A systematic reduction in the absorbance signal was reported (4) for Ag with a progressive increase in U concentration up to 20 mg/mL. A study on the atomization of Ag in matrix-free solutions as well as in the (Pu+Th)/ (U+Th) matrix was, therefore, carried out. The variation obtained in the GFAAS absorbance signal of Ag as a function of an increase in matrix concentration ranging from 0-40 mg/mL is shown in Table IV. As can be seen, a suppression in the absorbance signal was observed with an increase in matrix concentration ranging from 0-40 mg/mL. This indicates suppressive interference on Ag due to the presence of (Pu+Th)/ (U+Th) matrix. To meet the Ag expected specification limit of 2-10 ppm for AHWR fuel, the matrix concentration was kept at 20.0 mg/mL for further studies. The suppression in Ag absorbance with 20.0 mg/mL (Pu+Th)/ (U+Th) is almost 2.5 times that of the matrix-free solution.

All experimental parameters were freshly optimized for each of the 3%Pu+Th and 3%U+Th matrix. The maximum S/N ratio was obtained and the parameters are listed in Table V.

TABLE IV

Variation of Absorbance With Matrix Concentration on Ag Absorbance in 3%Pu+97%Th and 3%U+97%Th

Matrix Conc. (mg/mL)	Absorbance 3%Pu+Th		Absorbance 3%U+Th	
	Matrix Blank	Ag (0.04 µg/mL)	Matrix Blank	Ag (0.04 µg/mL)
0.0	0.002	0.740	0.00	0.740
1.0	0.031	0.590	0.012	0.582
2.0	0.033	0.572	0.005	0.454
5.0	0.036	0.446	0.006	0.405
10.0	0.037	0.388	0.007	0.410
20.0	0.036	0.386	0.022	0.426
30.0	0.023	0.361	0.012	0.419
40.0	0.024	0.357	0.022	0.406

TABLE V

Optimized Experimental Parameters of Graphite Furnace Atomizer for Ag in (3%Pu+Th)/(3%U+Th)

For 3%U+Th GF-3000			For 3%PU+Th CRA-63	
Temp. (°C)	Time (s) Ramp	Hold	Temp. (°C)	Time (s)
80	5	10	150	30
120	10	10	300	30
300	5	10	700	40
600	0.2	10	2300	3
2300	0.9	0.3		
20	14.5	10.0		

Peak profiles were plotted at 0.04 $\mu\text{g/mL}$ Ag in the absence and presence of matrix (3%U+Th and Th alone) at 20 mg/mL matrix concentration (see Figure 1).

It was observed that the peak profile broadens. Peak height and peak area reduces in the presence of the matrices as compared to matrix-free solutions. An enhancement of ~12% in peak profile of the (3%U+Th) matrix was obtained as compared with the Th matrix alone. To analyze the Pu-bearing samples, a Varian Techtron Model AA-6 atomic absorption spectrometer, equipped with a carbon rod atomizer (CRA-63, Mini Massmann, which is not computer-controlled), was used; hence, peak profile data for (3%Pu+Th) could not be obtained.

Successive loadings of (Pu+Th) and (U+Th) solutions leads to matrix build-up inside the graphite atomizer. However, this build-up of matrix did not have any significant effect on the Ag (0.04 $\mu\text{g/mL}$) absorbance with repetitive loadings of the 20.0 mg/mL mixed matrix on the same atomizer. The absorbance

remained constant with repetitive loadings of the sample for 100 atomization cycles.

Measurements of atomic absorption signals for Ag were carried out over a wide range of concentrations using standard solutions for these matrices. The linear analytical ranges in the presence and absence of the matrices were obtained and are shown in Figure 2.

Suppression in absorbance was observed for Ag in (3%Pu+Th) and in (3%U+Th) matrices as compared to the aqueous matrix. The influence of the mixed matrices on silver atomization behavior is also compared in Figure 2 with the reported data on the Th (5) matrix. The Ag sensitivity is poorer in mixed matrices in comparison to the pure nitrate solution, but better than that in pure thorium nitrate solution. The enhancement was found to be more pronounced in the (Pu+Th) than in the (U+Th) matrix as compared to Th matrix alone. It was reported earlier (3) that the presence of the plutonium matrix significantly altered the situ-

ation for Ag atomization and the Ag absorbance was improved as compared with a pure uranium matrix. This can be explained on the basis of thermal decomposition of $\text{Pu}(\text{NO}_3)_4$ which led to a marginal change in the oxygen-to-metal ratio as compared with $\text{UO}_2(\text{NO}_3)_2$ and, hence, Ag atomization was not affected in the Pu matrix. A similar explanation is also valid for the present studies with (Pu+Th) as compared to (U+Th).

These results necessitated the development of two independent analytical methods. Studies were carried out using a 3%Pu/Pu+Th and a 3%U/U+Th matrix. The analytical ranges and the lowest absolute amounts determined for each of the matrices of 3%Pu/(Pu+Th) and 3%U/(U+Th) are given in Table VI. The limits of quantitative determination obtained in the present work for 3%Pu/(Pu+Th) and 3%U/(U+Th) along with the reported data for Ag in the Th matrix are also included in the Table VI. The present values for Ag in the mixed matrices are lower by a factor of 2 than those

Fig. 1. Peak profile variation at 0.04 $\mu\text{g/mL}$ Ag in the absence and presence of matrix (3%U+Th and Th alone) keeping a total matrix concentration of 20 mg/mL.

Fig. 2. Analytical curves for Ag in aqueous, Th, (3%U+Th) and (3%Pu+Th), keeping a total of 20 mg/mL matrix concentration.

reported for the Th matrix. The characteristic concentration values obtained for Ag in the 3%Pu/(Pu+Th) and 3%U/(U+Th) matrices as evaluated from the calibration plots are also shown in Table VI. The corresponding characteristic concentration values obtained in the reported data for aqueous (3) and thorium (5) matrix solutions are also included in Table VI. Silver showed a reduction in its absorbance to varying degrees in the presence of the 3%Pu/(Pu+Th) and 3%U/(U+Th) matrices in comparison to matrix-free solution.

Using the standardized procedure, three synthetic samples were analyzed. The results obtained from the analysis of these synthetic samples with (3%Pu+97%Th) and (3%U+97%Th) are shown in Table VII. The replicate analyses of the synthetic samples showed the precision of the method to be better than 8% RSD.

CONCLUSION

In this work, accurate and precise methods were developed for the direct determination of Ag in nuclear grade 3%Pu/(Pu+Th) and 3%U/(U+Th) oxide by graphite furnace atomic absorption spectrometry (GFAAS). The effect of matrix composition was studied and an increase in Ag absorbance of 15% and 12% was obtained with (3%Pu+Th) and (3%U+Th) matrix, respectively, as compared with Th matrix alone.

The Ag absorbance remained unaffected with an increase in Pu/U concentration ranging from 2–4% mixed matrix. The expected percentage of Pu/U in Advance Heavy Water Reactor (AHWR) fuel is 2–4%. The variation in the GFAAS absorbance signal of Ag as a function of increase in matrix concentration in the range 0–40 mg/mL was studied. Based on the data,

determination of Ag at the 0.1 ppm level is possible in the presence of 100 µg amounts of matrix; however, it is necessary to have matching standards and sample compositions as regards the matrix concentration.

Since (Pu+Th) and (U+Th) oxides are refractory in nature, their lattices affect the atomization of silver. These nuclear materials are highly radioactive and highly toxic, and adequate suction was provided by the instrumentation for containment and to remove any toxic vapors from the glove box.

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Table VI
Analytical Results for Determination of Ag
in Pu+Th and U+Th Matrices and Characteristic Concentrations
of Ag in (Pu+Th) and (U+Th) and in Aqueous Th Matrix

Linear analytical range in 3%Pu/(Pu+Th) and 3%U/(U+Th) matrix	Limit of Quantitative Determination (pg)			Characteristic Concentrations**			
	3%Pu/(Pu+Th)	3%U/(U+Th)	100% Th (5)	Aqu. (3)	100% Th (5)	3%Pu/(Pu+Th)	3%U/(U+Th)
0.002–0.08 µg/mL							
0.1–4.0 ppm*	10	10	20	0.2	0.55	0.52	0.53

*Based on 100 µg of Pu+Th and U+Th in 5-µL solution.

**Characteristic concentration is defined as the concentration corresponding to an absorbance of 0.0044.

TABLE VII
Results of Analysis of Three Synthetically Prepared Samples for the
Determination of Ag at ppm Levels in Pu+Th and U+Th Matrices

Sample No.	Concentration of Spike (ppm)			% RSD
	Added	Obtained		
1.	0.8	0.77	0.775	8
2.	1.5	1.51	1.45	7
3.	2.5	2.34	2.35	4

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