Studies on Matrix Interference and Atomization Behavior of Al, Cr, Cs, Cu, Mn, Ni and Zn in Th Matrix Using GFAAS Technique

Paru J. Purohit*, Neelam Goyal, and S.V. Godbole
Radiochemistry Division, Bhabha Atomic Research Centre,
Trombay, Mumbai 400085, India

INTRODUCTION

Atomic emission spectrometric (AES) methods using inductively coupled plasma (ICP) and D.C. Arc excitation sources are capable of providing multi-element determination. These methods used for trace metal analysis of nuclear materials (U/Th/Pu matrices) involve either the chemical or physical separation of the major matrix, followed by determination of the analytes by AES methods. Chemical separation procedures based on solvent extraction for the separation of the major matrix from the analytes are usually preferred while using inductively coupled plasma as an excitation source (1,2). Physical separation procedures based on volatility differences between the analytes and the matrix are used with the help of a suitable carrier and D.C. Arc as an excitation source (3,4). However, these methods suffer from drawbacks such as poor precision in case of D.C. Arc-AES and requiring large sample sizes with ICP-AES.

Electrothermal atomization atomic absorption spectrometry (ETA-AAS) combined with graphite furnace (GF) is a proven technique for the direct determination of a number of trace elements in various matrices using small sample sizes without the need of separation of the major matrix (5-9). The most significant factors that influence the atomization in graphite furnace include the analyte-carbon and matrix-carbon interactions and

ABSTRACT

An electrothermal atomization atomic absorption spectrometric (ETA-AAS) method with a graphite furnace (GF) atomizer has been developed for the direct determination of Al, Cr, Cs, Cu, Mn, Ni, and Zn in a thorium matrix without prior chemical separation of the matrix. The influence of thorium matrix on the atomization behavior of the analytes and the effects of varying matrix concentrations were investigated.

The studies revealed a significant reduction in the analyte signal due to the presence of thorium and its magnitude increased with Th concentration. Multielement solution standards with graded concentrations of the analytes and fixed concentrations of the matrix were used in the standardization process. Based on these investigations, analytical methods were developed for the direct determination of these analytes. The absolute lowest amount determined was, Al and Zn - 5 ng; Cu and Cr - 0.05 ng; Mn - 0.2 ng; and Cs and Ni - 0.25 ng. Repeatability ranged from 4-10% RSD for all of the analytes. Thorium accumulation within the atomizer over its repetitive use did not cause any significant change in the absorbance signals up to 100 atomization cycles.

The analytical results were obtained for spiked samples having analytes added at three different concentration levels based upon the analytical ranges established. The estimated values were in close agreement with the added amounts within the range of precision.

oxygen release (10,11). The influence of carbon is more pronounced when analytes are to be determined in the presence of refractory matrixes forming stable carbides. Even though the matrix frequently causes interference in practical analysis procedures, successful trace metal determination of many of the elements in refractory matrixes such as U-Pu (5), U-Th (8), and U (6,9) has been reported.

India has vast reserves of thorium (Th) and the three-stage Indian nuclear program is based on the utilization of thorium for production of fissile ^{233}U in the Fast Breeder Reactor (FBR), Pressurized Heavy Water Reactor (PHWR), and Advanced Heavy Water Reactor (AHWR). Hence, trace metal characterization of Th becomes an essential feature for its use as a nuclear material (12). In the present work, studies were carried out for the development of GFAAS-based methods for the determination of Al, Cr, Cs, Cu, Mn, Ni, and Zn in Th matrix using small sample sizes without chemically separating the matrix. The studies include investigation of the effects on analyte absorbance due to the presence of the matrix, its concentration, and accumulation inside the furnace.

EXPERIMENTAL

Instrumentation

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 in these studies.

*Corresponding author.
E-mail: parupurohit@yahoo.co.uk
Tel. No. 9122 25590630
Fax No. 9122 25505151

The AAS unit was adapted for radioactive work by modifying the modular setup by placing the isolated atomizer in a glove box environment (13). Single-element hollow cathode lamps were used for each of the analytes. The operating current for HCL, the spectral bandwidth, and the analytical wavelengths used for each of the elements are given in Table I.

Reagents and Chemicals

All of the reagents used were of analytical grade purity. Quartz double-distilled water (Q.D.D.) was used for the preparation of the standards and sample solutions. The high purity chemicals, procured from Johnson-Matthey (U.K.), were used for preparation of the elemental solutions (2 mg/mL) by dissolving the appropriate amounts of respective metal or compound in HNO₃ for Cr, Cs, Cu, Mn, Ni, and Zn. Aluminum was dissolved in concentrated HCl and subsequently converted into nitrate medium.

The working standards were prepared by appropriate dilution of the elemental solution using 0.1 M HNO₃ and stored in PVC vials to prevent any contamination from the glass. Thorium (200 mg/mL) was prepared by dissolving weighed amounts of high purity oxide in a concentrated HNO₃+HF (0.03M) mixture. The solution was evaporated to near dryness, repeatedly treated with concentrated HNO₃ for removal of HF, and finally made up to volume.

Standards and Samples

Two sets of standards, each containing graded amounts of analytes in the concentration range of 0.001–20.0 µg/mL, were prepared in aqueous solution and also with 20 mg/mL of Th matrix. Another set of solutions, having a fixed concentration of analyte and varying concentrations of Th in the range 0–100 mg/mL, were prepared to investigate the matrix effects.

TABLE I
Instrumental Parameters

Element	Wave-length (nm)	HCL Current (mA)	Spectral Bandwidth (nm)
Al	309.2	5	0.5
Cr	425.4	10	0.5
Cu	324.7	10	0.2
Cs	853.0	20	0.5
Mn ^a	403.1	10	0.5
Ni	232.0	15	0.75
Zn ^a	307.6	10	0.5

Deuterium continuum lamp was operated at 25 mA.

^a Less sensitive analytical line.

Three synthetic samples were prepared from E. Merck (Darmstadt, Germany) high purity ICP solutions (1 mg/mL) for each of the elements (Al, Cr, Cs, Cu, Mn, Ni, and Zn) in 20 mg/mL thorium covering the full range of analysis.

Procedure

The experimental parameters were optimized in order to obtain the maximum signal-to-noise ratio reproducibly. Atomizer heating was carried out in the dry, pyrolysis, and atomization stages and heating took place in the step mode. A 5-µL sample aliquot was used for each determination.

Thorium interference was investigated by varying the Th concentration from 0–50 mg/mL at the intermediate concentration of each of the analytes. In this way, the Th concentration that could be tolerated to obtain the optimum absorbance signal was established. Subsequently, the matrix buildup/accumulation effect was studied by successively loading and atomizing the sample in the same atomizer for about 100 atomization cycles, i.e., up to 10 mg of Th. For all of the elements, the most sensitive analytical lines were used, except for Zn and Mn where less sensitive analytical lines were used. These analytes showed a high absorbance value

even for quartz-distilled water. The analytical response for each analyte was studied by analyzing samples prepared from E. Merck reference standards. All measurements were carried out in peak height mode.

RESULTS AND DISCUSSION

Effect of Th Matrix

The atomization of an analyte in GFAAS is influenced by the analyte matrix and carbon matrix interactions. It contributes to the matrix effect and also forms one of the important aspects to be studied prior to the development of a new analytical procedure. In the presence of Th, the absorbance was found to suppress significantly in comparison to that obtained in aqueous solution. Hence, the present work deals with the studies on the atomization behavior of a few analytes (Al, Cr, Cs, Cu, Mn, Ni, and Zn) in the presence of Th matrix.

The experimental parameters such as pre-atomization and atomization temperatures were optimized for all of the analytes in a matrix-free solution and in the presence of Th matrix. The dry temperature for the aqueous solution was optimized at 300 °C for smooth and complete drying of the sample without causing any sputtering. In the absence of any matrix, pyrolysis temperature is not required. Hence, 300 °C (dry temperature) for 5 seconds (minimum time) was used for pyrolysis in aqueous solution. It was found to provide better atomization signals.

In the thorium matrix, the effect of pyrolysis temperature was studied in the 300–900 °C range. In the Th blank solution, the pyrolysis temperature and time were optimized to 800 °C and 40 seconds, respectively. This was based on the observation that a lower temperature resulted in higher non-specific absorbance due to the incomplete decomposition of the Th matrix. At

800 °C / 40 seconds ash conditions, the background signal for the Th 'blank' reduced significantly and resulted in an improved S/N ratio. Similarly, the effect of atomization temperature on analyte absorbance was investigated in the 1800 to 2700 °C range. In order to obtain a better signal/noise ratio for subsequent studies, an atomization temperature of 2550 °C for the atomization of Cr, Cs, Cu, Mn, and Zn was used and 2700 °C for Al and Ni.

Possible non-specific absorbance from Th, examined by using a D₂ continuum lamp, was found to be negligible for all of the analytes using optimized conditions for the dry, pyrolysis, and atomization stages. The blank absorbance signal for each of the analytes at 20 mg/mL Th concentration was found to be of the order of 0.01–0.02 at the analytical lines used. However, in case of Cu, blank contribution from thorium was high. This was due to HF, which was used in dissolution of ThO₂ and was found to be impure with respect to Cu.

To ascertain the extent of interference due to the presence of thorium, the absorbance signal for each of the analytes at intermediate concentrations was measured in the presence of varying concentrations of thorium. The magnitude of suppression in the absorbance signal was studied by measuring the absorbance as a function of Th concentration in the range of 0–50 mg/mL. The relative change in absorbance signal as a function of thorium concentration for all of the analytes is shown in Figure 1. The absorbance was reduced with increasing Th concentrations, but its magnitude varied with the analytes. As can be seen from the Figure 1, with an increase in Th concentrations up to 20 mg/mL, the absorbance signal for Cu, Cr, Cs, and Ni reduced by 30–60%, thereafter it stabilized. Zinc and Mn showed a sharp decrease, i.e., 50%

even with 1 mg/mL of Th, while Al showed as high as 80% reduction in absorbance signal at 20 mg/mL Th. With a further increase in Th concentration there was only a marginal change in the absorbance for Al, Mn, and Zn. All studies were, therefore, carried out at the 20 mg/mL Th concentration.

It was necessary to ensure that the suppression in absorbance was due to the presence of Th matrix. The absorbance signals for each of the analytes at intermediate concentrations in aqueous solution and in the presence of thorium matrix (20 mg/mL) were measured under identical ash conditions. The absorbance values obtained in aqueous solution at a pyrolysis temperature of 300 °C (aqueous condition) and 800 °C (Th condition) and in thorium matrix at 800 °C pyrolysis temperature are shown in Table II. As can be seen, absorbance in the aqueous solution at 300 °C and 800 °C did not show any significant

difference; however, in the presence of Th (20 mg/mL), the absorbance was significantly reduced. This indicated that the suppression in absorbance signal was due to the presence of Th matrix and not due to the loss of analytes at higher pyrolysis temperatures.

The reduction in absorbance signal could be due to various reasons:

(a) *Deterioration of Atomizer Surface*

On repeated use, the atomizer deteriorates as the carbon layer of the tube is depleted due to the formation of ThC₂. This leads to sample seepage from the tube wall and reduces the absorbance signal. The formation of ThC₂ was confirmed by XRD studies where residue was collected from the furnace after a number of atomization cycles (Figure 2). Further, it was observed that loading of 10 µL xylene prior to each atomization

Fig. 1. Absorbance as a function of Th concentration.

cycle resulted in partial restoration of the absorbance signal. These observations suggest that seepage can partly account for the reduction in absorbance.

(b) Increased Partial Pressure of Oxygen

ThO_2 is known to form gaseous thorium monoxide, $\text{ThO}_{(g)}$, at 1700 °C and above and ThC_2 at above 2170 °C with release of [O] and CO, respectively (14-16). ThO is stable only in the gaseous state.

TABLE II
Effect of Pyrolysis Temperature and Presence of Th Matrix on Absorbance Signal

Element	Concentration	Absorbance Signal in Aqueous Solution	Absorbance Signal Under Identical Condition in Aqueous and Thorium matrices	
	($\mu\text{g/mL}$)	Aqueous (300°C)	Aqueous (800°C)	Th (800°C)
Zn	5.0	0.498	0.497	0.249
Cu	0.04	0.840	0.820	0.300
Cr	0.08	0.389	0.385	0.250
Al	1.0	0.780	0.795	0.060
Mn	0.2	1.280	1.170	0.600
Cs	0.2	0.600	0.620	0.380
Ni	0.4	0.480	0.450	0.200

absorbance signal in varying concentrations of Th. Absorbance reduces with an increase in Th concentration (Figure 1). This indicates that at higher matrix concentrations, more of the analyte atoms are trapped and absorbance is reduced. However, at 20 mg/mL of Th concentration, the absorbance signal was affected most. A further increase in Th concentration did not have any significant effect on absorbance.

(d) Formation of Intermetallic Compounds

Apart from the increased partial pressure of oxygen and analyte entrapment in the matrix lattice, the high degree of suppression in the case of Al (in comparison to other elements) is attributed to the formation of large numbers of Th_xAl_y type of inter-metallic compounds with Th. The Th_2Al_3 type of compound (TM=1394 °C) forms eutectoid (19) and further reduces the absorbance for Al.

Our studies indicated that the suppression in absorbance in the Th matrix is a composite effect

mainly due in part to an increase in partial pressure of oxygen in the presence of thorium matrix which is due to the release of oxygen during thermal decomposition of thorium nitrate to thorium oxide (14-16) and analyte entrapment in the stable matrix lattice. In addition, formation of intermetallic compounds is one of the factors, relevant only in cases where the analyte is known to form these types of compounds with Th. Tube deterioration affects the absorbance but to a smaller extent.

Effect of Th Accumulation

Since the same atomizer is used for a number of atomization cycles and Th accumulates inside the furnace, the effect due to Th buildup in the furnace on analyte absorbance was studied using 20 mg/mL Th concentration. The change in absorbance signal, as a function of atomization cycles for Cr as model element representing all the other elements, is shown in Figure 3. This was studied by measuring the absorbance at an intermediate analyte concentration, initially up to

30 atomization cycles, then at a regular interval of 10 atomization cycles for about 100 atomizations. Accumulation of matrix did not have any significant effect on the absorbance signal for about 100 atomization cycles. In the initial 5 to 6 atomization cycles, reproducibility was found to be poor; however, the overall spread in the absorbance signal was within the limit of variation, i.e., 10% RSD.

Analytical Results

Using the optimized parameters, the analytical procedure was adopted for the determination of these analytes in a 20 mg/mL Th matrix. A high matrix blank for Cu restricted the matrix concentration to 10 mg/mL. To standardize the method, the absorbance signals were measured for all of the analytes using two sets of standards: one containing graded amounts of analytes in a 20 mg/mL Th matrix; the other free from thorium. Analytical plots for Cu as a model element in aqueous and thorium matrices are presented in Figure 4. As can be seen from this figure, the slope

Fig. 3. Influence of matrix accumulation as a function of atomization cycles.

Fig. 4. Analytical plot for Cu in aqueous and Th matrices.

TABLE III
Optimized Experimental Parameters
and Analytical Results in Th (20 mg/mL) Matrix

Ele- ment	Atomization Temp./Time	Linear Analytical Range	Absolute Amount Detected	Sensitivity	Regression	
	(°C)/(s)	(µg/mL)	(ppm)	(g)	Abs./5ng	
Al	2700/4	1.0 - 10.0	50 - 500	5 x 10 ⁻⁹	0.034	0.99920
Cr	2550/4	0.01 - 0.2	0.5 - 10	5 x 10 ⁻¹¹	2.7	0.99911
Cu	2550/3	0.01 - 0.06	1.0 - 6.0 ^a	5 x 10 ⁻¹¹	8.05	0.99948
Cs	2550/3	0.05 - 0.5	2.5 - 25	2.5 x 10 ⁻¹⁰	4.5	0.99997
Mn	2550/3	0.04 - 0.6	2.0 - 30	2.0 x 10 ⁻¹⁰	1.56	0.99902
Ni	2700/4	0.05 - 0.7	2.5 - 35	2.5 x 10 ⁻¹⁰	0.62	0.99819
Zn	2550/3	1.0 - 15.0	50 -750	5 x 10 ⁻⁹	0.055	0.99958

Pre-atomization temperature/time: 800 °C/40s.

ppm: Based on 20 mg/mL Th. ^a ppm: Based on 10 mg/mL Th.

TABLE IV
Results of the Analysis of Synthetic Samples in Th Matrix

Element	Amount Added	Amount Estimated	RSD	Element	Amount Added	Amount Estimated	RSD
	(µg/mL)	(µg/mL)	(%)		(µg/mL)	(µg/mL)	(%)
Al	2.50	2.51	8.4	Ni	0.06	0.085	6.9
	3.50	3.40	4.5		0.15	0.145	7.1
	5.00	4.82	7.6		0.30	0.305	3.8
Cr	0.02	0.02	5.2	Cs	0.03	0.033	4.3
	0.06	0.07	4.9		0.15	0.134	3.1
	0.10	0.105	6.2		0.40	0.450	3.8
Cu	0.015	0.017	9.0	Zn	1.50	1.520	8.2
	0.040	0.043	3.5		4.00	4.00	2.9
	0.06	0.065	2.9		12.0	11.7	2.8
Mn	0.05	0.05	8.0				
	0.30	0.315	5.0				
	0.50	0.485	3.0				

of the analytical curve in the Th matrix is significantly reduced compared to the aqueous/matrix-free solution. This indicated a reduction in sensitivity and absorbance in the presence of Th. The analytical results, such as atomization temperatures, linear analytical range, lowest possible amount that could be detected in Th matrix, and the sensitivity calculated from the analytical plots, are shown in Table III. The lowest amount deter-

mined for Cr in Th was 0.5 ppm, whereas for Al and Zn it was 50 ppm.

The effect due to the presence of 21 common metallic elements (Ag, Al, B, Ba, Be, Cd, Cr, Cs, Co, Cu, Fe, Li, Mn, Mo, Na, Mg, Ni, Si, Sn, Ti, V, and Zn; other than the element of interest) on analyte absorbance was studied. These are the elements normally present and required to be determined in fuel and fuel materials. The presence of

these elements at concomitant levels did not show any significant effect on the absorbance signals.

The performance of the analytical method was evaluated by analyzing three synthetic samples for each of the analytes prepared from the high purity elemental solution (E. Merck, Darmstadt, Germany), covering the entire range of analysis with optimized matrix concentrations. The results of the analysis of these samples based on 10 replicate measurements are shown in Table IV and are in good agreement with those expected. The precision of the method was determined for each of the analytes at different concentration levels of the samples. The relative standard deviation calculated from 10 replicate measurements was found to be better than 10% RSD. It was observed that the addition of matrix deteriorates the atomizer. This leads to irreproducibility of the results. Ten microlitres of xylene loaded prior to each atomization cycle (20) prevents seepage losses through the graphite surface and helps in obtaining reproducible results.

CONCLUSION

The optimized electrothermal atomization atomic absorption spectrometry (ETA-AAS) method with a graphite furnace (GF) atomizer can successfully be utilized for the direct determination of Al, Cu, Cr, Cs, Mn, Ni, and Zn in a thorium matrix without any matrix separation. The absolute lowest amount determined was Al and Zn at 5 ng; Cu and Cr at 0.05 ng; Mn at 0.2 ng; and Cs and Ni at 0.25 ng. Repeatability ranged from 4 to 10% for all of the analytes. The analytical results were obtained for spiked samples having analytes added at three different concentration levels based upon the analytical ranges established. The estimated values were in close agreement with the added amounts within the range of precision.

The presence of matrix suppresses the analytical signal to varying degrees. The observed suppression in absorbance signal in the presence of thorium matrix is due in part to an increase in pressure of the oxygen released from the dissociation of large amounts of ThO₂ and/or entrapment of analyte atoms in a stable thorium oxide, carbide lattice. In addition, absorbance is also suppressed due to a deterioration of the atomizer surface. The effect due to the formation of intermetallic compounds is relevant only in cases where the analyte is known to form such compounds.

Based on the results of this study, the determination of these analytes at ppm levels is possible in the presence of a thorium matrix. Since signal suppression is dependent on thorium concentration, appropriate standard/sample matching with respect to thorium concentration is essential for sample analysis.

ACKNOWLEDGMENTS

The authors sincerely show their gratitude to Dr. V.K. Manchanda, Head, Radiochemistry Division, for his keen interest and constant encouragement during the course of this work. The authors are also thankful to Dr. (Mrs.) Meera Keskar for providing us XRD results for the Th samples.

Received December 1, 2010.

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