Influence of Uranium, Thorium, and Zirconium Matrices on Silver Absorbance in Graphite Furnace Atomic Spectrometry (GFAAS)

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ABSTRACT

The present studies were taken up to understand the influence of uranium, thorium, and zirconium matrices on silver absorbance in graphite furnace atomic absorption spectrometry (GFAAS). The absorbance signal of Ag in the presence of uranium (U), thorium (Th), and zirconium (Zr) matrices is significantly reduced compared to that in a matrix-free solution. To understand the effect of matrix on the Ag absorbance signal, the atomization mechanism of Ag was studied in the aqueous, U, Th, and Zr matrices. In aqueous, U, and Th matrices, carbothermic reduction of Ag_2O is followed by the vaporization of Ag_0 at a lower temperature, while at a higher temperature the Ag trimer is the precursor to free atoms. In a Zr matrix, at low temperature, Ag atoms are formed by dissociation of gaseous silver fluoride [AgF_g], while at a higher temper-

ature mode of atomization it is the dissociation of the Ag dimer. Formation of AgF in a Zr matrix is due to the presence of fluoride ions which result from the HF solution used in the Zr matrix dissolution. The activation energies and the mode of atomization do not change in aqueous, uranium, and thorium matrices, while in a Zr matrix it changes due to the presence of fluoride ions. Signal appearance temperature increases in the matrix compared to matrix-free solution.

Reduction in the absorbance signal in the presence of the matrix was correlated to the possibility of physical trapping of the analyte in the stable matrix lattices, increased partial pressure of oxygen in the furnace, reduced active carbon sites, formation of inter-metallic compounds in case of a Th matrix and, to a lesser extent, due to tube deterioration with high matrix loading.

stage resulting from the formation of volatile compounds (2,6). However, it is reported that chemical modifiers can be useful to overcome such problems (2). Recently, Peter et al. (7) effectively used *in situ* matrix separation for the determination of a few analytes in soil samples. In our laboratory, we developed analytical methods using a graphite furnace atomizer for a number of common metallic elements in nuclear materials such as plutonium (Pu) (8), uranium (U) (9), thorium (Th) (10,11), and Zr (12), where the matrix is found to affect analyte absorbance.

During the development of these analytical procedures it was observed that for most of the elements, the absorbance signal was significantly reduced in the presence of U, Th, and Zr (8-12) matrices as compared to matrix-free solutions. Uranium, thorium, and zirconium are known to form refractory oxides and/or carbides and their effect on these analytes is not yet fully understood. Silver absorbance was also reduced significantly in the presence of these matrices. The present studies are, therefore, aimed at trying to understand the suppression in silver absorbance in the presence of these matrices and whether the atomization mechanism plays a role in absorbance suppression or if any other factors are responsible for the suppression in the absorbance signal.

A number of reports are available on the investigation of the atomization mechanism in aqueous solutions using various approaches, such as the kinetic (13), thermodynamic (14), and combined kinetic-thermodynamic approach (15).

INTRODUCTION

Atomic absorption spectrometry (AAS) is one of the important techniques used in all analytical laboratories working on trace metallic assays 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 requiring only a significantly

small sample size. ETA-AAS makes use of metal, graphite, and many other types of atomizers (1). ETA-AAS with a graphite furnace (GF) atomizer suffers physical, chemical, and ionization interferences, which includes loss of volatile elements, reduced analyte volatility in the presence of the matrix, and/or a tendency for carbide formation (1,2). In particular, these types of interference studies are done for geological (3) and biological samples (4,5). The signal reduction in the majority of cases was identified as losses during the pre-atomization

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Also, by measuring the partial pressure of oxygen (16,17) and through adsorption-desorption of the analyte from the atomizer surface (18, 19), the atomization mechanism of the particular analyte can be studied. In the present studies, we adopted the combined kinetic-thermodynamic approach to understand the atomization mechanism. The studies include the determination of signal appearance temperature (T_{app}) and activation energy (E_a) for atom formation in all of the matrices.

EXPERIMENTAL

Instrumentation

A Model GBC 906 atomic absorption spectrometer (GBC Scientific Equipment, Australia), equipped with a GF-3000 power supply, GF-3000 graphite furnace atomizer, and deuterium lamp background correction system, was used for analyte atomization. Details of the AAS instrument and preparation of the U and Th matrix solutions are reported earlier (20,21).

Chemicals and Solution Preparations

Uranium and thorium concentrations in the standard solution were 20 mg/mL. High purity Ag solution (1 mg/mL) was procured from E. Merck, Darmstadt, Germany. A zir-

conium matrix solution was prepared by dissolving zirconium oxide (189 mg) in concentrated hydrofluoric acid in a platinum crucible and evaporating to dryness. Zirconium fluoride (ZrF_4) thus formed was dissolved in 2 mL of water and finally made up to 10-mL volume with 0.1 M HNO_3 . Due to the poor solubility of ZrF_4 (14 mg/mL) (22), the Zr concentration in the standard solution was 10 mg/mL. A Model M/s Raytek two-color optical pyrometer (Raytek Corporation, USA), sensitive in the range of 1000–3000 °C, was used to measure the temperatures in the atomization stage.

Procedure

The detailed analytical procedure adopted in our laboratory for the determination of Ag in U, Th, and Zr matrices was reported earlier (9–12). The heating parameters, optimized for Ag in the aqueous as well as U/Th/Zr matrices to ensure complete atomization so that the absorbance profile reaches to the base line, are listed in Table I. A cleaning step was introduced to ensure that there is no memory effect. During the optimization it was also ensured that there is no pre-atomization loss of an analyte. The absorbance signals for Ag in uranium at different pre-atomization temperatures are listed in Table II.

The activation energies and appearance temperatures for the atomization mechanism were determined from the Arrhenius plots of $\ln(A)$ vs. absolute T^{-1} . Arrhenius plots were obtained from the absorbance-time-temperature profile of the absorbance signal. The slope of the plot is equal to $-E_a/R$, where E_a is the activation energy (15). These values were compared with the reported thermodynamic data and used to understand the mechanism. The graphite furnace temperatures were measured by focusing the optical pyrometer through the sampling hole, assuming that the black body conditions persisted. The set and measured temperatures were in good agreement. All absorbance measurements were carried out in peak height mode, which is the most commonly used signal measurement in analytical AAS since it provides better sensitivity. Walter Slavin (23) recommended the use of the platform technique for peak area measurements in GFAAS analysis. However, Slavin also mentioned that peak area measurements are not suitable where analytes are vaporized from the furnace wall. During the present work, the analyte was vaporized from the furnace wall; hence, the measurements were carried out in peak height mode.

TABLE I
Atomization Temperatures for Ag in Aqueous, U, Th, and Zr Matrices

Aqueous Solution			U/ Th/ Zr Matrices		
Temperature (K)	Ramp Time (s)	Hold Time (s)	Temperature (K)	Ramp Time (s)	Hold Time (s)
253	10	15	253	10	15
453	10	15	453	10	15
573	10	15	573	10	15
2473	1.0	0.3	973	2	30
2573	0.1	0.2	2573	0.8	0.3
			2673	0.1	0.2

TABLE II
Effect of Pre-atomization Temperature on Ag Absorbance in U Matrix (atomization temperature : 2573 K)

Pre-atom. Temp.(K)	Ag Absorb. ^a	RSD (%)	Blank Absorb. ^a	RSD (%)	Net Absorb. ^a
573	0.399	36	0.110	15.0	0.289
673	0.386	40	0.088	14.6	0.298
773	0.385	23	0.084	14.0	0.301
873	0.316	8.0	0.065	17.0	0.241
973	0.255	2.9	0.050	4.0	0.205
1073	0.217	2.4	0.046	3.0	0.171

^a Absorb. = Absorbance.

RESULTS AND DISCUSSION

During the development of analytical methods for a number of elements, it was found that the absorbance signals for the analytes in U/Th/Zr matrices were significantly reduced in comparison to those in aqueous solution (9-12). In the present studies, during optimization care was taken to ensure that there is no pre-atomization loss of Ag (Table II). As can be seen, with an increase in pre-atomization temperature the absorbance signal increased with an increase in blank contribution. Though the net absorbance was high at a lower pre-atomization temperature, the blank absorbance also increased with poor reproducibility. This is probably due to the incomplete decomposition of the matrix at temperatures lower than 973K. A similar trend was observed in the Th and Zr matrices. Therefore, in further studies, the pre-atomization temperature used was 973K. This also indicates that there are no pre-atomization losses and suppression in absorbance could be due to the presence of the matrix.

To understand the matrix suppression effect, the absorbance signal for Ag (0.04 µg/mL) was

measured in uranium for a repeated number of atomization cycles and compared with the signal obtained in aqueous solution. Figure 1 shows the absorbance signals obtained for Ag in aqueous solution in the first atomization cycle and subsequent signals in uranium matrix. There is a significant suppression even in the first loading of the U matrix. In subsequent loadings, the signal was reduced further and obtained nearly a constant/stable value after 8 to 12 atomizations. A similar effect was observed for other matrices. The suppression in the first loading of the matrix suggests that suppression occurs due to the presence of the matrix rather than due to a change such as deterioration of the atomizer surface.

The typical absorbance profile for Ag in all of the matrices is shown in Figure 2. Due to signal broadening in the U/Th/Zr matrices, the absorbance signals were

measured both in peak height (maximum absorbance) and peak area mode (integrated absorbance from peak start to peak end) after 10 atomization cycles; i.e., after the absorbance signal has stabilized. An increase in peak width can be attributed to slow analyte release and, in such cases, peak area is a better mode of measurement. With this in view, the absorbances were measured both in peak height and peak area mode and are listed in Table III. It can be seen that the absorbance was reduced even in peak area mode, suggesting that the suppression is not only due to a slow release of analyte affecting peak height absorbance, but there is a net signal reduction which is reflected in peak area mode also. This indicates that the matrix plays a major role in signal suppression. To understand the change in atomization efficiency, the reaction mechanism was studied in the presence and absence of these matrices.

TABLE III
Absorbance Values for Ag in Peak Height and Peak Area Mode

Absorbance	Aqueous	Uranium	Thorium	Zirconium
Peak Height (A)	0.664	0.315	0.196	0.460
Peak Area (A.s)	0.156	0.138	0.059	0.116

Fig. 1. Suppression in absorbance signal in presence of matrix (uranium). First absorbance: aqueous solution, subsequent absorbance: U.

Fig. 2. Absorbance profile for Ag in aqueous, uranium, thorium, and zirconium matrices from peak_{app} to peak_{end}

Atomization Mechanism of Ag From Aqueous-Nitrate Solution

The atomization temperature for Ag in aqueous solution is 2473K, while in U, Th, and Zr it is 2573K. The sample is loaded in the form of AgNO₃. Decomposition of AgNO₃ is reported to take place as follows (16, 22, 24):

The Ag metal (condensed) is likely to be formed by dissociation of solid silver oxide at around 673K, much below the appearance temperature (1208K) of Ag. L'Vov (16) measured the partial pressure of oxygen and reported the dissociation of Ag₂O into Ag atoms and O₂ molecules. Aggett and Sprott (25) measured the vapor pressure of Ag from Ta ribbon and graphite filament atomizers. The minimum vaporization temperature of Ag, from both atomizers, was the same with the vapor pressure of 1.33x10⁻² Pa. These reports indicated that oxide dissociation precedes atomization.

Campbell and Ottaway (14) predicted that metal atoms are formed directly in the gaseous state following carbothermic reduction of the oxide. However, Frech et al. (26) reported the volatilization of condensed Ag, where the reduction step precedes volatilization. The T_{app} (1208K) and E_a obtained in the present work, along with the data from the literature in aqueous solutions, are listed in Table IV. In most of the cases, the single E_a value (nearly 260±25 KJ/mole) suggests the sublimation/vaporization of Ag_(s/l); while Buhay et al. (19) and Rojas et al. (18,27) obtained two E_a values: vaporization/sublimation of Ag metal at lower temperature and cluster dissociation at higher temperature.

TABLE IV
T_{app} and E_a Values for Ag in Aqueous Medium: Obtained in Present Studies Compared With Those Reported in Literature

Sr. No.	T _{app} (K)	E _a (KJ/mole)	Ref. No.	Sr. No.	T _{app} (K)	E _a (KJ/mole)	Ref. No.
1	1150	-	14	8 ^a	-	237/124	26
2	1130	255	17	9	-	292	28
3 ^a	-	239/125	18	10	-	250	29
4	-	220	19	11	1053	252	30
5	-	252	22	12	1120	269	31
6	1123	-	24	13	1050	272	32/17
7	1050	-	25	14 ^a	1208	244/119	Present

^aTwo precursor mechanism.

There are a number of publications dealing with the thermodynamics and kinetics of thermal decomposition of Ag₂O, yet the real mechanism of Ag₂O decomposition has not been fully established. However, prior to atomization, the presence of condensed silver in the furnace is reported by a number of researchers (17,18,26-33). Free energy changes for oxide dissociation and carbothermic reduction of silver oxide (34) (at the temperatures where reaction becomes spontaneous) are shown below:

Eq. 2a

Eq. 2b

Negative ΔG° suggests that both reactions (2a, 2b) are spontaneous. However, ΔG° for carbothermic reduction reaction takes place at a much lower temperature than oxide dissociation; carbothermic reduction of Ag₂O looks more favorable and leads to the formation of Ag metal.

At appearance temperature (1208K), Ag is in Ag_(l) form. The melting point of Ag is 1233K. The Arrhenius plot for silver in aqueous solution in the present studies is

shown in Figure 3a. Two intersecting segments indicate that two mechanisms are involved in the formation of free atoms. The temperature of intersection is 1323K. E_a, 244 KJ/mole, is in agreement with the heat of vaporization (22) of Ag at low temperature, while E_a, 119KJ/mole, agrees well with the dissociation of the trimer [Ag_{3(g)}] (35,36) at higher temperature. With an increase in temperature, Ag clusters are formed which are dissociated to Ag atoms at a higher temperature. The cluster is identified as trimer [Ag_{3(g)}] on the basis of its dissociation energy. The atomization mechanism proposed in aqueous solution is the vaporization of Ag_(l) at lower temperature, while dissociation of Ag_{3(g)} at higher temperature is preceded by carbothermic reduction of the oxide.

It was rather strange to observe that the Ag absorbance increased with xylene treatment even with a new/fresh atomizer. However, xylene loading prior to atomization is helpful in preventing seepage losses due to prolonged use of the

atomizer. The average of five absorbance values was obtained from the new atomizer with and without use of xylene prior to sample loading (see Table V). Signal intensity was improved by 60% in the aqueous matrix, while 20–30% in the U and Th matrices with the use of xylene prior to sample loading. This can probably be attributed to a higher number of active carbon sites due to xylene loading, which in turn helps to increase the carbothermic reduction process and effectively improves signal intensity. This further confirms that in the aqueous, U, and Th matrices, carbothermic reduction plays a pre-dominant role prior to the formation of Ag atoms.

Atomization Mechanism of Ag From U, Th and Zr Matrices

E_a plots for silver in all of the matrices are shown in Figures 3a, b, c, and d. The appearance temperature and activation energies deter-

mined in the aqueous, U, Th, and Zr matrices are listed in Table VI. E_a in the U and Th matrices are nearly the same as in aqueous solution. This indicates that there is no change in the atomization mechanism in the U and Th matrices. The E_a values for Ag in the Zr matrix are higher compared to those obtained in the aqueous, U, and Th matrices. This suggests that the atomization mechanism is quite different for the Zr matrix.

It is to be noted that the Zr solution contains both NO_3^- and F^- ions, suggesting the possible role of the fluoride ion during the atomization process. The heat of formation for AgF and AgF_2 is -204.82 and -51 KJ/mole, respectively. Even though the formation of AgF_2 is more favorable, it decomposes to AgF at 973K and can be a likely precursor in the atomization process. The activation energy obtained at a lower temperature ($<1736\text{K}$) is 369 KJ/mole, which is in close agree-

ment with the bond energy of $\text{AgF}_{(g)}$ (22), while at a higher temperature ($>1736\text{K}$), E_a 151KJ/mole matches well with the dimer (34) dissociation. In addition, the boiling point of AgF is 1435K, while T_{app} for Ag in the Zr matrix is 1550K, which supports that AgF is in gaseous form. Thus, the mode of atomization in Zr is dissociation of $\text{AgF}_{(g)}$ at lower temperature, while at higher temperature dimer $[\text{Ag}_{2(g)}]$ dissociation is the preferred mode of atomization. Following is the reaction mechanism in the Zr matrix:

Higher E_a in Zr corresponds to the smaller cluster size and increased cohesive forces of the atoms in the clusters. In the Zr matrix, xylene treatment was not significant as in this case fluoride dissociation is the mode of atomization.

Signal Suppression in the Presence of Matrix

E_a in aqueous/U/Th matrices suggests that the mode of atomization has remained the same and does

TABLE V
Effect of Xylene on Silver Absorbance
Average Absorbance (five measurements) for Ag (0.04 µg/mL)
With and Without (W/O) Xylene Loading

Atomization	Aqueous	Uranium	Thorium	Zirconium
W/O Xylene	0.359	0.471	0.281	0.419
With 10 µL Xylene	0.579	0.526	0.372	0.428

TABLE VI
 T_{app} and E_a Values for Ag in Aqueous, U, Th, and Zr Matrices in Present Studies

Matrix	Atom. Temp. (K)	T_{app} (K)	Inter- section (K)	Activation Energy E_a (KJ/mole)	
				Lower Temperature	Higher Temperature
Aqueous/Nitrate	2473K	1208±50	1323	244±9	110±12
Uranyle Nitrate	2573K	1421±60	1578	$\text{Ag}_{(l)}$ vaporization	$\text{Ag}_{3(g)}$ dissociation
				261±8	110 ⁵
Thorium Nitrate	2573K	1390±60	1530	$\text{Ag}_{(l)}$ vaporization	$\text{Ag}_{3(g)}$ dissociation
				273±8	122±8
Zr (HF + HNO_3)	2573K	1550±40	1736	$\text{Ag}_{(l)}$ vaporization	$\text{Ag}_{3(g)}$ dissociation
				369±10	151±8
				$\text{AgF}_{(g)}$ dissociation	$\text{Ag}_{2(g)}$ dissociation

not explain the suppression in the absorbance signal in the presence of the matrix. The reduction in the absorbance is in the order Th>U>Zr. The most probable reasons for absorbance suppression, which can be applied to most of the oxide-containing matrices, are as follows:

Reduced Active Carbon Sites

Increased oxygen concentration (Eq. 5a, 6a) due to the decomposition of large matrix concentrations (compared to that in aqueous solution and formation of U/Th carbides, Eq. 5b, 6b) reduces the active carbon sites, affects the carbothermic reduction process, and in turn the atom density for the AA signal.

Physical Trapping

As seen from the absorbance profile, Th has maximum suppressive effect (70%) compared to U (45%) and Zr (25%). The matrix concentration in the GF is 100 µg/aliquot, while that of Ag is at nanogram level. It is likely that Ag atoms are physically trapped in the stable thorium-uranium matrix lattice (10). The relatively lesser degree of suppression observed in the Zr matrix can probably be due to a smaller (10 mg/mL) amount of matrix used. Moreover, the average linear thermal expansion coefficient (37) for ThO₂ (9.32x10⁻⁶ °/C) is less than for UO₂ (10.52x10⁻⁶ °/C) in the temperature range of 298–1273K. Release of trapped atoms from the ThO₂ matrix lattice will be much slower and more difficult than from the UO₂ matrix lattice, causing larger suppression.

Inter-metallic Compounds

Formation of Ag-Th inter-metallic compounds (38) with eutectic temperatures less than or equal to the appearance temperature of Ag, i.e., ThAg₃ (1163K), ThAg₂ (1178K), and Th₂Ag (1230K), suggests that significant suppression in case of Th in the absorbance signal can also occur due to the formation of inter-

Fig. 3. E_a plots for Ag in different matrices (a) aqueous, (b) uranium, (c) thorium, (d) zirconium.

metallic compounds. U and Zr do not form an inter-metallic compound with silver.

Furnace Deterioration

Suppression of the absorbance signal due to deterioration of the graphite furnace cannot be ruled out (39). The atomizer surface is affected due to carbide formation and an increase in oxygen content, which leads to a reduction in active carbon sites and is chemical in nature. On the other hand, the effect due to surface deterioration resulting from repeated use of the furnace for more than 50 atomization cycles leads to seepage losses of the sample and is physical in nature. The latter effect also leads to signal suppression but to a lesser extent and after a prolonged use of the atomizer. However, a signal suppression in the presence of the matrix right from the first atomization cycle indicates that suppression due to tube deterioration cannot be the major cause.

Thus, suppression in the absorbance signal of U, Th, and Zr matrices is a composite effect of all the factors mentioned above and cannot be explained fully by any one of the effects. In the present studies, the signal appearance temperature in the U, Th, Zr matrices is higher than from aqueous solution (Table VI). This can be due to increased partial pressure of oxygen (17,40), which reduces the active carbon sites and shifts the absorbance signal to a higher temperature.

CONCLUSION

In this study, the effect of the presence of the matrix (U, Th, and Zr) on Ag absorbance and its atomization mechanism was investigated using a graphite furnace atomizer. The atomization mechanism in aqueous/U/Th solutions is the vaporization of $\text{Ag}_{(l)}$ at lower temperature, while dissociation of

$\text{Ag}_{3(g)}$ at higher temperature preceded by carbothermic reduction of the oxide. In case of a Zr matrix, the mode of atomization is dissociation of $\text{AgF}_{(g)}$ at lower temperature, while at higher temperature dimer dissociation is the preferred mode of atomization. The atomization mechanism does not have any significant effect on signal absorbance. Suppression can probably be due to an increased partial pressure of oxygen and formation of stable matrix carbides, which reduces the active carbon sites affecting the carbothermic reduction and also physical trapping of the analyte in the stable matrix lattice. Though to a lesser extent, suppression due to tube deterioration cannot be ruled out. Formation of Ag-Th eutectoids in the thorium matrix causes relatively large suppression compared to U/Zr matrices. No such compounds are reported in U and Zr matrices. This work is useful for laboratories working in the field of spectrochemical analysis of nuclear fuels.

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