Insight Into Electrothermal Atomization Mechanism of Several Transition Metals (Cr, Cu, Mn, Ni, Zn) in Uranium and Thorium Matrices: GFAAS Study

Santosh Kumar Gupta*, S.K. Thulasidas, P.J. Purohit, Neelam Goyal, and S.V. Godbole
Radiochemistry Division, Bhabha Atomic Research Centre
Trombay, Mumbai, 400085, India

INTRODUCTION

Atomic absorption spectrometry utilizing an electrically heated graphite furnace as the atomization device has proven to be a very successful method for the direct determination of a number of important trace elements in nuclear material-based samples (1-6). This advantage could become universal only if the chemical interferences that occur for some elements could be nullified. These studies showed that the absorbance signal observed for all of the analytes in pure uranium (U) (7-11) thorium (Th) (5,12) or mixed uranium + thorium matrices (2,4,13) was suppressed compared to that observed for pure matrix-free solutions. This necessitates a complete understanding of the atom formation mechanism with and without the matrices and also the factors influencing this process. In addition to the suppression in the magnitude of the analyte signal and the changes in the useful analytical life of the graphite furnace, surface studies were also taken up to understand the changes occurring in the surface composition and morphology of the atomizer.

In view of the importance of uranium and thorium, work has been carried out on the atom formation of Cr, Cu, Mn, Ni, and Zn in aqueous, uranium, and thorium matrices. The quality control of uranium- and thorium-based nuclear materials is essential as uranium is used as a nuclear fuel in Pressurized Heavy Water Reactors (PHWRs), thorium

ABSTRACT

To understand the reason behind the suppression of analyte absorbance in the presence of uranium and thorium matrices, studies were taken up to understand the reaction mechanism for Cr, Cu, Mn, Ni, and Zn analytes with and without matrices. Reaction mechanisms were proposed for atom formation using Arrhenius plots. Investigations reveal that the activation energies for these analytes in uranyl and thorium nitrate solutions are similar to those obtained in pure aqueous solutions and, hence, similarity in the atomization mode for all of these elements. With a view to understanding the suppressive effect due to the matrix, investigations were carried out using scanning electron microscopy (SEM) on the products formed on atomization for Cr, Cu, Mn, Ni, and Zn in aqueous, uranium, and thorium matrices. The investigations reveal that uranium and thorium matrices react with the graphite atomizer surface, leading to the formation of an uneven surface which affects the atomization efficiency, while an aqueous solution does not create any defect on the surface.

is used as a blanket material in Fast Breeder Reactors (FBR), and U+Th is the proposed fuel for Advanced Heavy Water Reactors (AHWR) (14).

India has vast reserves of thorium (Th) and the three-stage Indian nuclear program is based on the utilization of thorium for pro-

duction of fissile ^{233}U in the Fast Breeder Reactor (FBR) and use of $(\text{Th-U}^{233})\text{O}_2$ as a fuel in the Advanced Heavy Water Reactor (AHWR). Hence, trace metal characterization of Th becomes an essential feature for its use as a nuclear material. Past studies were carried out for the development of GFAAS-based methods for the determination of Cr, Cu, Mn, Ni, and Zn in a Th matrix using small sample sizes without chemically separating the matrix. Likewise, quality control of U and U+Th is carried out for use with Pressurized Heavy Water Reactors (PHWR) and the proposed fuel for Advanced Heavy Water Reactors (AHWR). The studies include investigation of the effects on analyte absorbance due to the presence of the matrices, its concentration, and accumulation inside the graphite furnace atomizer. Elements such as Cr, Ni, etc. are generally monitored to check for process pick-up and the conditions of the process equipment. The presence of Ni in high concentrations also leads to problems in sintering. Low melting elements such as zinc, if present, will cause liquid metal embrittlement altering the fuel structure and causing failure. The presence of Cu, Mn, and Zn is monitored to ensure the total impurity content mentioned within the specified limit and also to ensure the individual impurity content under specified limits. In general, the presence of light elements results in a change in density and reduction in fissile content. It is, therefore, necessary to characterize nuclear materials for trace metallic constituents as part of their chemical quality control (CQC).

*Corresponding author.
E-mail: santosbg@barc.gov.in

The electrothermal atomization mode in atomic absorption spectrometry (ETA-AAS) displays high atomization efficiency on several counts, such as efficient sample introduction, compact size of atomizer, and fairly uniform higher temperature as compared to flame systems. The electrothermal atomization mode, however, makes complete description of the atom formation mechanism more difficult due to an increase in the number of interfering species, which are chemical in nature. The studies on atomization processes reported in the literature (15–19) are all carried out on analytes with water or weak acids with a zirconium matrix (6). However, the reaction mechanism on the basis of activation energies (E_a) calculation using Arrhenius plots is not yet reported for Cr, Mn, Ni, Cu, and Zn in uranium and thorium matrices using the GFAAS technique. The nature of the reaction mechanism in the presence of matrices such as U and Th gets altered because of various interactions taking place in the graphite atomizer viz. analyte-carbon, analyte-matrix and carbon-matrix. These interactions are bound to influence the atomization process to varying degrees, which in turn affect the analytical results.

The aim of the present study is to understand the reason for the change in the analyte absorbance signals with a change in matrix on the basis of the mode of atomization and the possible intermediate reaction sequence. These studies give an insight into the relation between the atoms formed and their precursors during atomization. It is well documented that analyte absorbance reduces in the presence of these matrices (1,4,6). The basic atomization mechanism involved in these studies, for some of the analytes, appears to be through carbothermic reduction and, for some, through oxide dissociation prior to atomization.

EXPERIMENTAL

Instrumentation

To study the atomization mechanism in U and Th matrices, a computer-controlled GBC-906 atomic absorption spectrometer, equipped with a GF 3000 graphite furnace atomizer (GBC Scientific Equipment Pvt., Ltd., Australia), was used. The details of the instrument are provided in Table I and reported earlier in detail (1).

The atomizer was covered with a shield consisting of a Perspex® sheet which could be removed when access to the atomizer was necessary. Containment of uranium and 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 (see Figure 1).

TABLE I
Instrumental Parameters

Instrumentation	GBC-906 AAS
Graphite furnace	GF 3000 GFA
Spectral bandwidth	0.5 nm
Lamp fill gas	Ne
Gas used	Ar
Flow rate	6 L/min
Lamp current	15 mA

The morphological investigations of the products formed on the graphite atomizer surface were carried out using a scanning electron microscope (SEM). This was done on an instrument having both an Everhart-Thornley, UK, secondary electron detector and a solid state back-scattered electron detector. The micrographs were taken at 20–30 kV acceleration voltages.

Standard Solutions and Reagents

Details of the sample preparation are given earlier (6) for the uranium (200 mg/mL) and thorium (200 mg/mL) solutions. Analyte solutions were prepared by appropriate dilution of the standard stock solutions (Cr, Cu, Mn, Ni, and Zn) of 1 mg/mL in 5% nitric acid (VHG Labs., Manchester, NH, USA). The instrumental parameters used for these analytes are reported elsewhere (5). Argon gas of 99.995% purity was used as the purge gas.

The following experiments were carried out for all of the analytes using a programmable heating cycle and a computerized signal recording system. Absorbance-time and temperature-time profiles were obtained simultaneously as a computer output.

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

Effect of Matrix on Signal Appearance Temperature (T_{app})

The profiles were obtained using different temperature settings on the GF-3000 control unit. From the initial portion of the profile at various temperature points, corresponding absorbance signals were measured at a fixed analyte concentration. The lowest temperature, where a detectable signal was obtained above the blank signal, was taken as the appearance temperature (T_{app}) (16) in the aqueous, uranium, and thorium matrices.

Determination of Activation Energies for Atom Formation

For a fixed concentration of the analyte, the atomization temperature was measured from T_{app} onwards. The corresponding absorbance signals were measured for different temperatures, and a plot of logarithm of the absorbance as a function of the inverse of the absolute temperature was obtained. It should normally yield a straight line with the slope of an Arrhenius plot giving the activation energy. The free atoms in the gaseous state are formed either through oxide dissociation or carbothermic reduction of the oxides (if Gibbs' free energy change is negative at T_{app}) (18). Hence, with a free energy change, the melting/boiling points of analyte/analyte oxides are the guidelines for understanding the basic reaction mechanism. The procedure was repeated for all of the analytes in the aqueous as well as the uranium and thorium matrices.

Temperature Measurements in the GBC-906 GF 3000

In the GBC-906 GF 3000 unit, the temperatures are set for any absorbance measurement and are not monitored during measurements, so the actual temperatures are not known. In activation energy calculations, an error in temperature can lead to erroneous results for the atomization mechanism.

Keeping this in view, temperature measurement studies were carried out in the range of 1000–3000 °C. The temperatures were set on the instrument using programmable heating parameters and measured using a Model M/s Raytek two-color optical pyrometer (Raytek Inc., USA), sensitive in the range of 1000–3000 °C, and providing a fast response. There was exceptionally good agreement between the set and measured temperatures in the 1000–2800 °C range. However, beyond 2800 °C, there was a ± 100 °C error in the measured temperature. These temperatures were used in the E_a calculations and for studying the reaction mechanism. The activation energies and T_{app} were, in turn, compared with those reported in the literature to infer the final mode of atomization.

Scanning Electron Microscope Experiments

For surface studies, graphite atomizers were treated with the matrix heated to 2700 °C for 40 atomization cycles. Separate atomizers for each of the matrices were prepared by loading 5 μ L of (a) 0.1 M HNO_3 , (b) uranyl nitrate (20 mg/mL), (c) thorium nitrate

(20 mg/mL), and (d) 300 atomization cycles with 0.1 M HNO_3 . Surface erosion was studied using SEM on the residue collected after heating the atomizer with the solutions.

RESULTS AND DISCUSSION

In order to understand the factors responsible for suppression in the absorbance signal, the atomization mechanism was investigated for all of the analytes with and without matrices. The atomization mechanism was studied using the thermodynamic approach as published by Sturgeon et al. (20). From the initial portion of the time-absorbance profile (Figure 2), the Arrhenius plots were generated and the T_{app} and activation energies obtained for the atomization process involved. 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 the E_a value calculations were restricted to the initial few hundred milliseconds of the absorption profile (Figure 2, absorbance-time profile). Absorbance data taken from this region of the curve were used to construct the Arrhenius plots. The

Fig. 2. Typical absorbance-time profile showing the part of the curve from which the data were taken for chromium.

T_{app} obtained for all of the analytes in the presence of the three matrices along with the E_a values obtained are listed in Table II.

The T_{app} for Cr did not change much with the matrix, while for Cu, Mn, Ni, and Zn the changes observed were high. For the oxides to undergo carbothermic reduction, the free energy change per mole (ΔG°) should be negative at T_{app} . It was observed that the standard free energy change per mole (ΔG°) does not become negative at T_{app} for Mn and Zn, and hence, the carbothermic reduction does not become a thermodynamically favorable reaction. However, for Cr, Cu, and Ni the standard free energy change per mole (ΔG°) becomes negative at T_{app} , and hence, the carbothermic reduction becomes a thermodynamically favorable reaction.

Activation energy corresponding to a single slope or two slopes was obtained. Single slope, determined for Mn and Zn, corresponds to single activation energy value, whereas two slopes were obtained for Cr, Cu, and Ni corresponding to two activation energy values. The activation energies and T_{app} were compared with those reported in the

literature (21-23) to infer about the final mode of atomization. Two major pathways leading to gaseous-free atoms were identified: reduction of the analyte oxide by carbon or thermal dissociation of the metal oxide with subsequent sublimation/vaporization of the metal. The specific details of the atomization mechanism for each of the analytes in the presence and absence of matrices are discussed below.

Chromium

Chromium nitrate, $\text{Cr}(\text{NO}_3)_3$, heated under carbon rod atomizer (CRA) conditions, produces Cr_2O_3 . The appearance temperature obtained for Cr in nitrate solution is 1960 K. It is known that Cr_2O_3 is the most stable oxide of Cr at 1960 K (21) since the melting point of Cr_2O_3 is 2700 K. The free energy change for the carbothermic reduction process of Cr_2O_3 is negative at T_{app} ; hence, it is possible that Cr_2O_3 undergoes carbothermic reduction prior to its atomization. The reduction of the oxide by carbon at T_{app} is also given in the literature (20) as:

The Cr Arrhenius plot (Figure 3) shows two straight line segments with different slopes intersecting at the temperature of 2100 K. Two sequential atomization energies were obtained for Cr when the analyte is taken as nitrate solution. The values corresponding to two slopes are 98 ± 4 and 45 ± 5 kcal/mole, respectively, for lower and higher temperatures. The E_a value obtained in the lower temperature regions (< 2100 K) is in close agreement with the heat of sublimation of $\text{Cr}_{(s)}$ (22) and in the higher temperature regions (> 2100 K) close to dissociation of the dimer (23). The reported value by Gaydon et al. (23) is 44 kcal/mol. Below the T_{app} temperature, Cr_2O_3 is the most stable oxide of Cr and must be in solid state. Hence, the possible pathway for chromium atom formation is given as:

Initially, the concentration of $\text{Cr}_{2(g)}$ was very low and in equilibrium with the condensed phase metal. Hence, $\text{Cr}_{(g)}$ atoms were formed by the sublimation of $\text{Cr}_{(s)}$. With an increase in temperature, the concentration of $\text{Cr}_{2(g)}$ increases. At sufficiently high temperatures (> 2100 K), the bulk of the $\text{Cr}_{(s)}$ sublimates, and above 2100 K, the dimer dissociation was the dominant precursor to free atoms. A single activation energy of 99 kcal/mole (18) and 94 kcal/mole (24) was reported and no dimer species were observed by them. These authors proposed a single mechanism based on the sublimation of $\text{Cr}_{(s)}$ after the carbothermic reduction of $\text{Cr}_2\text{O}_{3(s)}$. The formation of $\text{Cr}_{2(g)}$ and its corresponding E_a value (45 kcal/mole) is reported by Gaydon et al. (23). However, Castillo et al. (25) reported two activation energies of 250 and 120 kcal/mole, corresponding to

TABLE II
 E_a Values Obtained With the Appearance Temperatures
With and Without U and Th Matrices

Element	T_{app} K			E_a (kcal/mole)		
	Aqu.	U	Th	Aqu.	U	Th
Cr	1960/1660 ^a	2030	2030	98 ± 4^b	94 ± 5^b	98 ± 3^b
				45 ± 5^c	50 ± 6^c	54 ± 6^c
Cu	1200/1270 ^a	1400	1400	80 ± 4^b	78 ± 3^b	79 ± 4^b
				46 ± 2^c	44 ± 2^c	40 ± 4^c
Mn	1480/1480 ^a	1800	1800	97 ± 4	93 ± 4	104 ± 6
Ni	1700/1590 ^a	1900	1900	99 ± 5^b	101 ± 8^b	97 ± 5^b
				46 ± 3^c	53 ± 3^c	45 ± 3^c
Zn	1140/1140 ^a	1340	1340	81 ± 3	83 ± 4	87 ± 6

^a Reported (20), ^b Lower temperature, ^c Higher temperature.

the thermal dissociation of $\text{Cr}_2\text{O}_{3(s)}$ to $\text{Cr}_{(g)}$ at low temperature, while in the higher temperature region it is a gas phase dissociation of monoxide (CrO).

The activation energies for Cr in uranyl and thorium nitrate solutions are similar to those obtained in pure nitrate solutions, suggesting that the mode of atomization remained the same. Therefore, the Arrhenius plot in nitrate solution (Figure 3) is for the first time published in this paper.

Copper

The Arrhenius plot (Figure 4) for the nitrate solution of Cu showed two straight line segments with a T_{app} of 1200 K. The slopes correspond to two atomization energies of 80 ± 4 and 46 ± 4 kcal/mole, intersecting at the temperature of 2100 K. The E_a values correspond to the heat of sublimation of $\text{Cu}_{(s)}$ and the Cu-Cu bond dissociation energies. Below T_{app} , $\text{CuO}_{(s)}$ (m.p. 1600 K) is formed (21) which undergoes a reductive decomposition of the oxide. It is a thermodynamically favorable reaction at 1200 K. The E_a values obtained in the lower temperature regions (< 2100 K) are in close agreement with the heat of sublimation of $\text{Cu}_{(s)}$ (81 kcal/mol) (22) and in the higher temperature

region (> 2100 K) dissociation of dimer (46 kcal/mol) (23).

Thermal dissociation of the metal oxide was reported by L'vov et al. (26) and Aggett et al. (27) for the formation of $\text{Cu}_{(s/l)}$ while Chang et al. (28) suggested that at T_{app} , $\text{Cu}_{(s/l)}$ is possible both by thermal dissociation and reduction by carbon of the copper oxide. Though thermal dissociation or carbon reduction of the metal oxide may be a matter of dispute, the presence of metallic copper on the graphite surface prior to its atomization was confirmed by all researchers. They reported that the carbothermic reduction is favorable at 1200 K and results in the atomization of various solid copper compounds with the average values at 360 kJ/mol (86 kcal/mol) and 180 kJ/mol (43 kcal/mol) (18).

In the present studies, the proposed mechanism is:

The activation energies for Cu in uranyl and thorium nitrate solutions remained the same as for pure nitrate solutions, which suggests

that the mode of atomization also remained essentially the same. The Arrhenius plot in aqueous solution (Figure 4) is, therefore, given. However, T_{app} increased by 200 K in the presence of uranium and thorium.

Manganese

When $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}_{(s)}$ is heated under GF atomizer conditions, $\text{MnO}_{(s)}$ is formed. The free energy change per mole (ΔG°) is positive T_{app} and, hence, the reduction of $\text{MnO}_{(s)}$ by carbon at T_{app} (1480 K) is not favorable. Below the T_{app} , Mn exists as $\text{MnO}_{(s)}$ on the graphite surface under the GF atomizer conditions where the melting point is reported as 1978 K (22). The Arrhenius plot for the atomization of Mn (Figure 5) shows a single straight line segment. The slope corresponds to the atomization energy of 97 ± 4 kcal/mole. The atomization energy of 97 ± 4 kcal/mole obtained for Mn in nitrate solutions corresponds to the bond dissociation energy of MnO . Weast (22) also reported that on heating, $\text{MnO}_{(s)}$ is decomposed prior to its vaporization or sublimation and, hence, the formation of $\text{MnO}_{(g)}$ at appearance temperature is completely ruled out and the dissociation energy of $\text{MnO}_{(s)}$ is 92 kcal/mol. Thus, the most probable reaction

Fig. 3. Arrhenius plot for chromium in aqueous solution.

Fig. 4. Arrhenius plot for copper in aqueous solution.

mechanism for the thermal dissociation of $\text{MnO}_{(s)}$ is as follows:

It can be seen that the reduction of $\text{MnO}_{(s)}$ by carbon at T_{app} (1480 K) is not favorable and, hence, the carbothermic reduction of $\text{MnO}_{(s)}$ is not possible. Chang (28) reported that $\text{MnO}_{(s)}$ undergoes carbothermic reduction around the T_{app} . In contrast, the experimental results by Sturgeon et al. (18) indicated that the precursor to the atomic vapor was $\text{MnO}_{(s)}$ and the bond dissociation energy is 390 kJ/mol (~93.3 kcal/mol). The findings in our study are supported by the results reported by Weast of 92 kcal/mol, Gaydon of 96 kcal/mol, and Sturgeon of 93.3 kcal/mol for the final mode of atomization.

The process leading to the atom formation of Mn appears to be affected by the uranium and thorium matrices only with an increase in T_{app} by approximately 200 K in comparison to pure nitrate solutions.

Nickel

The Arrhenius graph for atomization (Figure 6) of Ni shows two straight line segments with different slopes intersecting at a temperature

of 2200 K. Two sequential atomization energies were obtained at 99 ± 5 below 2200 K and 46 ± 3 kcal/mole above 2200 K. The T_{app} for nickel is 1700 K, less than the melting point of NiO (2263 K). Therefore, the oxide was considered to be present in the form of solid $\text{NiO}_{(s)}$. Gibbs' free energy change associated with the carbothermic reduction of NiO is negative at T_{app} . The E_a values probably correspond to the heat of atomization of $\text{Ni}_{(g)}$ and the dissociation energy of $\text{Ni}_{2(g)}$, respectively. To support our findings, we compared our data with the data from the literature. The formation of $\text{Ni}_{2(g)}$ was observed mass spectrometrically by Kant (29). Below T_{app} , $\text{NiO}_{(s)}$ is formed by thermal dissociation of the nitrate (21) and is readily reduced at T_{app} , since the free energy change is negative for the carbothermic reduction reaction of $\text{NiO}_{(s)}$ at T_{app} (30). This is likely to favor the formation of $\text{Ni}_{(s/l)}$ around the T_{app} . Since the melting point of Ni is 1720 K, Ni is present as Ni (see Eq. 5) on the graphite furnace. In the present studies, the energy of vaporization of $\text{Ni}_{(l)}$ is the heat of atomization for Ni at lower temperatures, while the energy associated with dissociation of $\text{Ni}_{2(g)}$ to $\text{Ni}_{(g)}$ atoms corresponds to higher temperatures. At low temperature, for-

mation of the Ni dimer appears to be less and its concentration increases with an increase in temperature. At sufficiently high temperature, most of the $\text{Ni}_{(l)}$ vaporizes, and beyond 2200 K, the dimer dissociation is the precursor to $\text{Ni}_{(g)}$ atoms. The formation of metal clusters or dimeric species of Ni was documented earlier (30). Thus, the most probable reaction mechanism is as follows:

The atom formation studies carried out by various researchers suggest that there exists a number of possible pathways for the production of $\text{Ni}_{(g)}$ atoms. Chang et al. (28) suggested that the production of Ni atoms through thermal decomposition and carbon reduction are spontaneous at T_{app} for Ni atoms and is also supported by L'vov (26). Brewer et al. (31) in their studies observed that the $\text{Ni}_{(g)}$ atoms are in equilibrium with solid diatomic $\text{NiO}_{(s)}$ at T_{app} . However, the energy required for this reaction is significantly higher than the values obtained in the present studies.

Fig. 5. Arrhenius plot for manganese in aqueous solution.

Fig. 6. Arrhenius plot for nickel in aqueous solution.

The reported data by Sturgeon of 102 kcal/mol and 55 kcal/mol (20) and Gaydon of 54.5 kcal/mol (23) support the evaluation of our study.

It may also be noted that $\text{NiO}_{(g)} 613 \text{ K} \rightarrow \text{Ni}_{(g)}$ and $\text{Ni}_{(s/l)} \rightarrow \text{Ni}_{(g)}$ have nearly the same E_a values. It is not easily possible to identify the unique pathway of atomization from E_a value alone. However, consideration of the feasibility of carbothermic reduction and the relative value of melting point and T_{app} serve as pointer to suggest that $\text{Ni}_{(s/l)} \rightarrow \text{Ni}_{(g)}$ takes place at lower temperature regions and dissociation of $\text{Ni}_{2(g)}$ at higher temperature regions.

The activation energies for Ni in uranium and thorium matrices are found nearly the same as in pure nitrate solutions. However, the appearance temperatures are higher by 200 K in the presence of uranium.

Zinc

The Arrhenius graph for atomization of Zn shows a single straight line segment (Figure 7). The slope corresponds to the atomization energy of 81 ± 3 kcal/mole. The thermogravimetric analysis of $\text{Zn}(\text{NO}_3)_2$ by Duval (21) shows that its monoxide is formed below the T_{app} (1140 K).

Reduction of the oxide by carbon is unfavorable below the T_{app} as reported by Sturgeon et al. (20). The dissociation of the oxide upon vaporization to $\text{Zn}_{(g)}$ is the major species in equilibrium with $\text{ZnO}_{(s)}$. It was also supported by Chang et al. (28) that at the T_{app} , the carbothermic reduction of $\text{ZnO}_{(s)}$ might take place even though the ΔG° for the process was reported to be positive at 1200 K. Reduction of the oxide by carbon is unfavorable below the T_{app} . $\text{Zn}_{(g)}$ must, therefore, result from the dissociation of $\text{ZnO}_{(s)}$. If we agree with regard to the carbothermic reduction, then the $\text{Zn}_{(g)}$ atoms formation must occur due either to sublimation of $\text{Zn}_{(s)}$ or vaporization of $\text{Zn}_{(l)}$. In either case, the E_a value should be around ± 30 kcal/mol.

$\text{Zn}_{(g)}$ must, therefore, result from the dissociation of $\text{ZnO}_{(s)}$. Dissociation of the oxide upon vaporization to $\text{Zn}_{(g)}$ is the major species in equilibrium with $\text{ZnO}_{(s/g)}$. The value of the activation energy of 81 ± 3 kcal/mole for the nitrate solution is in close agreement with the bond dissociation energy of $\text{ZnO}_{(g)}$ (83 kcal/mole) (22). Therefore, the most probable reaction sequence of atom formation appears to be:

Eq. 6

Before concluding that this is the most likely sequence for the atom formation of zinc, consider the following:

(a) The reported (22) melting point of $\text{ZnO}_{(s)}$ is 2512 K, which is much higher than the T_{app} , and means that $\text{ZnO}_{(s)}$ is subliming to $\text{ZnO}_{(g)}$.

(b) The CRA conditions are highly conducive for the reduction process; yet the carbothermic reduction does not play any role.

The activation energies for Zn in uranium and thorium matrices are found nearly the same as in pure nitrate solutions. However, the appearance temperatures are 160 K higher in the presence of uranium and 200 K higher in the presence of thorium matrix.

Matrix Effect

The atomization efficiency for the analytes under investigation is significantly lower in the presence of 100 μg uranium or thorium matrices. In spite of the higher atomization temperature, the suppression in absorbance signal persists in the presence of the matrices. The reduction in atom density may also be attributed to the surface activity of the graphite atomizer as reported earlier by Rogulskii et al. (32). Therefore, studies regarding surface morphology were carried out using Scanning Electron Microscopy (SEM) for surface studies for the products formed on atomization.

Scanning Electron Microscopy (SEM)

The changes in morphology of differently treated graphite atomizers used for U/Th matrices were studied using SEM which provides information on the physical state of the atomizer surface. SEM images

Fig. 7. Arrhenius plot for zinc in aqueous solution.

of the cross-section of a fresh atomizer, high temperature heated atomizer with 0.1 M HNO₃, and an atomizer treated with U and Th matrices were obtained by SEM and are shown in Figure 8 (a-e). Figure 8(a) shows the surface of an atomizer without any treatment, while Figure 8 (b-e) shows the tube surface after 40 atomization cycles on loading with 0.1 M HNO₃ (b), uranyl nitrate (c, d), and thorium nitrate (e). The SEM images revealed that the surfaces observed before treatment and after treatment with 0.1 M HNO₃ were almost similar to the new atomizer with slight roughening of the surface. In case of the U- and Th-treated atomizers, the original grain structure was destroyed and numerous small pits and pores were observed. These pits and pores may be produced on the surface of the atomizer due to interaction of the matrix with the graphite, leading to erosion of the layer.

A globule-like structure (protrusion) observed in uranium (Figure 8d) is probably due to the partial dissolution of UC/UC₂ and re-formation of the uranium carbide layer during repeated loading of the sample aliquot. Presence of UO₂ at 2700 °C also confirms re-dissolution

of UC₂ in the next aliquot loaded. This type of UO₂ dissolution on the atomizer was also reported by Hircq (33). The roughening of the surface leads to suppression in absorbance in the presence of uranium.

The suppression in absorbance was observed right from the first atomization of the new atomizer as well; and where there is no surface erosion, it can be assumed that suppression in the absorbance signal due to the atomizer deterioration cannot be the only cause.

The SEM image of the Th-treated atomizer (Figure 8e) is representative of a highly corrosive effect of Th with numerous pores and pits on the surface. No globule-like structure (protrusion) of thorium could be seen since dissolution of thorium essentially requires HF along with HNO₃. Hence, ThC₂ did not dissolve in HNO₃ during the next aliquot loading.

Eq. 8

These SEM data clearly show the formation of stable oxide/carbide lattices. These lattices are formed on the surface at a temperature of 1500 K and both uranium and thorium nitrates get converted into their respective dioxides (4). Similarly, the analytes get converted into their oxides, mostly dissolved in the main lattice of (Th/U)O₂/C. The diffusion rates of cationic elements in these lattices are very low. Thoria and urania lattices are very stable and have a defect-free structure due to their stoichiometric composition. Moreover, a fraction of the analytes dissolved in the (Th/U)O₂/C lattice, but considerably reduced their chemical activities, hence, their detectability. This is mainly due to the fact that nanogram amounts of analytes are being atomized in the presence of milligram amounts of uranium and thorium matrices.

The results of SEM showed that surface erosion occurred in the presence of U/Th matrices. This is mainly due to the carbonization reaction occurring on the surface. The observed changes in the T_{app} could not be directly correlated with the changes on the surface.

The observed changes in the T_{app} are explained with the help of absorbance vs. time profiles. Peak profiles for Cu, Cr, Mn, Ni, and Zn were plotted with and without uranium/thorium matrices. The three graphs within Figure 9 (a,b,c,d,e) represent 0 (matrix-free), 20 mg/mL U, and 20 mg/mL Th matrix concentrations for each of the elements.

It can be seen from the graphs that the peak profiles broaden and peak height reduces with the matrix as compared to the matrix-free solution. A large suppression in peak absorbance profile is seen with the matrix concentration. The

Fig. 8. SEM micrographs of the atomizer tubes: (a) without treatment, (b) 0.1 M HNO₃, (c) uranyl nitrate, (d) uranyl nitrate globule, and (e) thorium nitrate.

absorbance suppression in the analytes at 20 mg/mL is ~50% for almost all of the elements as compared to the matrix-free solution. It is also clear from the plots that the appearance of the signal is delayed as well as the peak height. The suppression in the signal is due to the delay in appearance signal and peak signal.

CONCLUSION

In this study, we have tried to understand the reason behind the suppression of analyte absorbance in the presence of uranium and thorium matrices. The mode of atomization remained the same irrespective of the matrices, therefore, studies regarding surface morphol-

ogy were carried out using Scanning Electron Microscopy (SEM). The changes in morphology of differently treated graphite atomizers used for U/Th matrices were found to be different. The results of SEM showed that surface erosion occurred in the presence of U/Th matrices. The SEM image of the Th-treated atomizer is representative of a highly corrosive effect of Th with lots of pores and pits on the surface and, hence, suppression in the analyte absorbance is more in the Th matrix. While a globule-like structure (protrusion) was observed in uranium, this is probably due to the partial dissolution of UC/UC₂ and re-formation of the uranium carbide layer during repeated loading of the sample aliquot.

It can be concluded that the mode of atomization remains essentially constant irrespective of the type of matrices present. Reduction in the absorbance signal can be due to the slowing down of the reaction kinetics in the atomization process with a high concentration of matrix. Analytes are in nanograms, while the matrix is in milligram amounts. Formation of stable matrix carbides on the inner surface of the atomizer blocks the analyte atoms and suppresses the atom density of the analytes. Surface roughening can markedly affect evaporation of the solution and will also lead to suppression in absorbance.

Fig. 9 (a,b,c,d,e). Absorbance vs. time profiles for the Cu, Cr, Mn, Ni, and Zn transition metals in aqueous, uranium, and thorium matrices.

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