Atomization Mechanism and Determination of Cd, Co, Cu, Mn, and Zn in Zirconium Matrix by GF-AAS Technique

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INTRODUCTION

Zirconium (Zr) and its alloys are important materials for the nuclear industry (1). Zirconium has a low neutron absorption cross-section for thermal neutrons, relatively good mechanical properties, excellent chemical compatibility with many corrosive media, favorable high temperature properties such as creep strength, resistance against stress rupture, and superior low temperature behavior. Due to these properties, Zr alloys, such as zircalloy-2, zircalloy-4, and Zr-Nb alloy, are used as cladding materials, and for calandria and pressure tubes for the reactor. Zr also plays an important role in the fabrication of a plate type fuel (Al-U alloy) by imparting the desired hardness to the fuel when added in small percentages. U-Zr alloys are developed for reactor applications due to their excellent corrosion-resistant and dimensional stability during thermal cycling. U-Th-Zr alloys are currently explored for use in research reactors. Recently, use of a U-Pu-Zr based fuel is being explored in experimental breeder reactor II (EBR II).

In addition, Zr has many non-nuclear applications. Zr-Nb alloys are used to make superconductive magnets. Its ceramic surface is used for total knee replacement in medical science. In the steel industry, it is used to remove nitrogen and sulfur from iron for enhancing the metallurgical property of steel, and when alloyed with iron it improves its machinability, toughness, and

ABSTRACT

In this work, the influence of the zirconium (Zr) matrix on Cd, Co, Cu, Mn, and Zn absorbance was studied when using a graphite furnace atomizer with atomic absorption spectrometric (GFAAS) analysis. The effect of Zr and its accumulation inside the furnace showed that absorbance is suppressed in the presence of the Zr matrix in comparison to a matrix-free solution. The probable reason for the suppression can be analyte entrapment.

The reaction mechanism involved in the formation of free analyte atoms in the aqueous as well as the Zr matrix was also studied. It was found that the atomization mechanism in both matrices remained the same for all of the elements studied, except for Cu. In aqueous solution, Cu undergoes carbothermic reduction of $\text{CuO}_{(s)}$, followed by sublimation of $\text{Cu}_{(g)}$ at a lower temperature, and dissociation of the Cu dimer ($\text{Cu}_{2(g)}$) at a higher temperature. In the Zr matrix, the precursor to free atoms was $\text{Cu}_{(s)}$. There was no indication of a dimer in the Zr matrix.

The lowest detection limit obtained after standardizing the method in the Zr matrix was as follows: Cd 0.05 ppm, Cu 1.0 ppm, Co 0.5 ppm, and Mn 1.0 ppm. Zn was determined using the 213.9 nm and 307.6 nm lines. The detection limits obtained were 5.0 ppm and 100 ppm, respectively. The reproducibility of the measurements ranged from 5–10% for the analytes listed. The methods developed can be utilized for the analysis of real samples without prior chemical separation of the zirconium matrix.

ductility. It is also used as a getter for vacuum tubes in flash bulbs and lamp filament. In both the nuclear and non-nuclear applications, the purity requirement of Zr is equally important.

Several reports have been published for the determination of some trace elements in Zr and ZrO_2 , mainly using inductively coupled plasma atomic emission spectrometry (ICP-AES) (2,3), inductively coupled plasma mass spectrometry (ICP-MS) (4,5), electrothermal vaporization (ETV)-ICP-AES (6,7), and atomic absorption spectrometry (AAS) using solid samples (8) and slurry samples (9). Electrothermal atomic absorption spectrometry (ETA-AAS) using samples in a solution form is a well-established technique for the determination of a number of impurities in a variety of matrices at microgram to sub-microgram levels. In particular, AAS with a graphite furnace (GF) atomizer has become a routine tool for trace metal characterization in cases where only small amounts of samples are available. In the present studies, graphite furnace atomic absorption spectrometric (GF-AAS) methods have been developed for the direct determination of Cd, Co, Cu, Mn, and Zn in a ZrO_2 matrix which meet the required specification limits.

The maximum permissible contaminant levels for nuclear-grade Zr, set by ASTM-B350/35M (10) for Cd, Mn, Co, and Cu, are 0.5, 50, 20, and 30 ppm, respectively. In spite of the phenomenal success due to the high atomization efficiency of the technique, the atom population and thereby analyte determination are affected severely in the pres-

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ence of different matrices (11,12). A study of analyte vapor generation in a GF atomizer is an important part of the development work to improve the performance of the technique. It is, therefore, essential to have proper knowledge about the processes involved in atomization of the analytes in the presence of the matrix. In the present work, attempts were made to develop analytical methods for the determination of Cd, Co, Cu, Mn, and Zn in a ZrO_2 matrix without chemical separation of the major matrix. In this context, studies were carried out to understand the effect of Zr on analyte absorbance and also the effect of accumulation of Zr in the graphite furnace.

EXPERIMENTAL

Instrumentation

In this study, a GBC-906 atomic absorption spectrometer (GBC Scientific Equipment Pty, Ltd., Australia), was used. The spectrometer was equipped with a GF-3000 power supply for the graphite furnace atomizer, using a heating rate as high as 2000 °C/s, and a deuterium lamp for background correction.

Single-element hollow cathode lamps (HCLs) were used for all of the elements, with the most sensitive analytical lines for the elements Cd, Co, and Cu; except for Mn and Zn, the less sensitive analytical lines were used due to the high reagent blank. An Eppendorf® variable volume micropipette was used to prepare the standard/sample solutions, while a 5- μL fixed volume autopipette was used for dispensing the sample/standard aliquots into the atomizer. Temperature-time-absorbance profiles of the absorbance signals, obtained after the atomization cycle, serve as the basis to study the atomization mechanism. A Model M/s Raytek (Raytek Inc., USA) two-color optical pyrometer,

sensitive in the range of 1000–3000 °C, was used to measure the temperatures in the atomization stage. The optical pyrometer was focused through the sampling hole assuming that black-body conditions persist. The set and measured temperatures were in good agreement.

Preparation of Standards and Samples

High purity chemicals, procured from Johnson-Matthey (UK), were used in the preparation of the elemental solutions (2 mg/mL). Appropriate amounts of the metal or compound were dissolved either directly in HNO_3 or first in HCl and subsequently by converting into nitrate medium. Due to the difficulty of dissolving ZrO_2 in nitric acid medium, the Zr matrix solution was prepared by dissolving appropriate amounts of high purity Zr oxide in HF and evaporating to dryness. The product obtained on evaporation was found to be ZrF_4 (see XRD pattern in Figure 1). Since ZrF_4 does not dissolve in nitric acid, it was dissolved in 2 mL of water and made up to 10 mL in 0.1M HNO_3 . Thus, the Zr solution contains both nitrate and fluoride ions.

All of the reagents used were of analytical grade purity. Quartz doubly distilled water was used in the preparation of the standard and sample solutions.

Two sets of standards, with concentrations of the analytes ranging from 0.0002–100 $\mu\text{g/mL}$, were prepared in the absence and in the presence of 10 mg/mL of Zr matrix. Due to the poor solubility (14 mg/mL) of ZrF_4 , the matrix concentration in the standards was maintained at 10 mg/mL for all studies. All solutions were stored in polyvinyl chloride (PVC) vials to prevent contamination from glass and to avoid adsorption losses.

Procedure

A 5- μL aliquot of an intermediate concentration standard containing 10 mg/mL (50 μg /aliquot) Zr was placed into the graphite furnace to optimize the heating parameters for reproducible signals. Since the atomizer is used repeatedly for a large number of atomization cycles, the effect of matrix accumulation inside the furnace was studied by successively atomizing the sample for about 100 atomization cycles. Peak height measurements were

Fig. 1. XRD Pattern for ZrF_4

carried out in 'gas stop' mode where during the atomization stage the purge (Ar) gas was stopped. The atomization mechanism was studied using the absorbance-time-temperature profile of the absorbance signal. From the initial portion of the profile at various temperature points, corresponding absorbance signals were measured. From these data points, the Arrhenius plot of log absorbance vs. inverse of absolute temperature was obtained and used to calculate the activation energies (E_a); signal appearance temperatures (T_{app}) were obtained from the absorbance profile. The appearance temperature is the temperature producing a just noticeable signal above the base line.

RESULTS AND DISCUSSION

Our earlier studies on the determination of Ag in U, Pu (11), and Al, Cr, Cs, Cu, Mn, Ni, and Zn in Th (12) matrices, indicated that the absorbance signals were significantly suppressed in the presence of these matrices compared to those in matrix-free or aqueous solutions.

Therefore, the effect of Zr on analyte absorbance also becomes an important factor to be studied in the determination of the analytes. The present work deals with the studies on the atomization behavior of Cd, Co, Cu, Mn, and Zn in the presence of the Zr matrix, and the results are compared with those obtained in aqueous solutions. These studies led us to ascertain that the interference was due to the presence of the Zr matrix.

Matrix Effect

Since the same atomizer was used for a number of atomization cycles, the matrix accumulates inside the furnace and can affect the analyte signal. Figure 2 shows the absorbance signal for Mn as a typical element, measured as a

function of the atomization cycles. The accumulated matrix inside the furnace up to 100 atomization cycles did not have any significant effect on analyte absorbance. A similar effect was observed for all the other analytes (Cd, Co, Cu, and Zn) of this study.

It was observed that in the presence of 10 mg/mL of Zr matrix, the absorbance signal for the analytes Cd, Co, Cu, Mn, and Zn reduced continuously during the first 6-8 atomization cycles. Subsequently, the absorbance signal stabilized. The stabilized absorbance signal for the Zr matrix was significantly reduced (40-70%) in comparison to the matrix-free solution. Hence, further studies were carried out after the signal stabilized. It was observed that with an increase in the Zr concentration ranging from 1-10 mg/mL (i.e., 1, 2, 5, 10 mg/mL), even after stabilized conditions, the absorbance was reduced with an increase in Zr concentration. This was probably due to the analyte getting trapped in the high matrix concentration.

Fig. 2. Absorbance as a function of atomization cycles.

Optimization of Pre-atomization and Atomization Temperatures

Pre-atomization (ash) and atomization temperatures are of prime importance for obtaining reproducible absorbance with the best signal-to-noise ratio. The pre-atomization temperatures in the aqueous and Zr matrices were optimized to achieve better reproducibility and to check the losses, if any, at this stage. In aqueous solution, the pre-atomization temperature was 573 K for smooth evaporation without loss of sample. However, for the Zr matrix, a higher pre-atomization temperature (873 K) was required for complete decomposition of the matrix (Table I).

The absorbance signals obtained at the two temperatures for aqueous solutions reveal that there are significant losses for Cd and Zn, moderate losses (30%) for Mn, while for Cu and Co the differences are marginal with an increase in pre-atomization temperature. Further comparison of the absorbance signals obtained at the same pre-atomization temperature (873 K) for the aqueous and Zr solutions revealed an increase in absorbance for Cd and Zn; however, the signals are still lower than the corresponding values obtained at 573 K in aqueous solution for the two analytes Cd and Zn. The absorbance signals are further reduced for Cu and Mn in the Zr matrix (in com-

TABLE I
Effect of Pre-atomization Temperature on Absorbance Signal in Aqueous and Zr Matrices

	Absorbance		
	Aqueous (573 K)	(873 K)	Zr (873 K)
Cd	0.674	0.019	0.320
Co	0.358	0.313	0.340
Cu	0.252	0.228	0.108
Mn	0.303	0.219	0.060
Zn	0.245	0.015	0.150

parison to the aqueous solution), while the change in Co signal is not significant. These findings suggest that in addition to pre-atomization losses, some other factors may be causing suppression in absorbance in the presence of the Zr matrix. Reduction in pre-atomization losses (increased absorbance) occurred for Cd and Zn, probably due to their physical trapping in the matrix and thereby preventing the losses, while for the analytes Co, Cu, Mn, and Zn similar physical trapping can have caused reduction. This behavior of the analytes explains that matrix plays a definite role in analyte atomization.

Similarly, the effect of atomization temperature on the absorbance signal was investigated in the temperature range from 1973 K to 2973 K. The temperature providing a maximum signal-to-noise ratio was used as the optimized condition for the atomization of each analyte. In order to understand the correlation between atomization temperature and analyte properties (such as bond dissociation energies), the melting and boiling points of the analytes/analyte oxides, and the atomization temperatures for each of the analyte, are listed in Table II.

During atomization in the furnace, the aqueous solution upon heating eventually gets converted to oxides. The order of bond disso-

ciation energies of these oxides is $\text{CoO} > \text{MnO} > \text{CuO} > \text{CdO} > \text{ZnO}$. The atomization temperatures followed a similar trend showing that minimum atomization temperature is required for Zn (which has the lowest dissociation energy), while maximum atomization temperature is required for Co (which has the highest dissociation energy). In general, a correlation is observed between bond dissociation energy and atomization temperature. However, it was also noted that the atomization temperatures were higher in the samples containing Zr in comparison to the aqueous solution.

In spite of the higher atomization temperature, there was a reduction in absorbance signal in the presence of the Zr matrix. In addition, with an increase in matrix concentration, the absorbance was reduced. This clearly indicates that the probable causes for the reduction in absorbance signal could be due to physical trapping of the analyte atoms in the matrix. However, there is the possibility of an additional factor responsible for the reduction in absorbance. In order to understand whether any other factor is responsible for the reduction in absorbance, the atomization mechanism was investigated in the aqueous solution and in the Zr matrix for all of the analytes studied (Cd, Co, Cu, Mn, and Zn).

Atomization Mechanism From Aqueous Solution

The atomization mechanism was studied using the well-established kinetic-thermodynamic approach used by Sturgeon et al. (13). The Arrhenius plots were obtained, and activation energies were calculated from the slope of the plot. Signal appearance temperatures were measured from the initial portion of the absorbance profile. Table III lists the appearance temperature and activation energy values obtained in the aqueous and the Zr matrix for Cd, Co, Cu, Mn, and Zn. Based on the T_{app} and E_a values, the proposed reaction mechanism for these elements are listed in Table III along with reported values (13) for comparison. In this study, the method of standard additions was not used. However, the matrix effect was studied in detail and the samples were analyzed using matching standards.

It is known that the metal atoms responsible for the absorbance signal are produced mainly through thermal dissociation or carbothermic reduction of the metal oxide (13) when the sample is atomized from nitrate medium. If the Gibbs' free energy change (ΔG°) for carbon reduction of the metal oxide is -ve at appearance temperature, it is considered that the reduction of the metal oxide by carbon is favorable. On the other hand, if ΔG° is +ve, oxide dissociation can be the probable mode of atomization. Hence, free energy change (13) and melting and boiling points of the analytes/analyte oxides (14) are taken as guides to understand the basic mechanism.

The free energy change for the carbothermic reduction of the Cd, Mn, and Zn oxides in the present studies was +ve at appearance temperature (13). In addition, the E_a values calculated from the Arrhenius plots for Cd, Mn, and Zn (Table III) agree well with the

TABLE II
Melting Point (M.P.), Boiling Point (B.P.), Bond Dissociation Energies, and Atomization Temperatures

	Element		Oxide		Bond Dissoc. Energy	Atomization Temp.	
	M.P.	B.P.	M.P.	B.P.		Aqueous	Zr
	(K)	(K)	(K)	(K)	eV	(K)	(K)
CdO	594	1038	1137	1832 s*	<3.8	2173	2473
MnO	1517	2235	1923	-	4.16±0.13	2673	2723
ZnO	693	1180	2248	-	2.8±0.4	2073	2173
CoO	2690	3143	2208	-	4.8±0.42	2773	2873
CuO	1356	2848	1599	-	4.1±0.3	2573	2673

*s = At this temperature, the compound sublimes.

energy required for dissociation of the gaseous metal oxides, which indicated that dissociation of the oxide is the probable mode of atomization. Since the melting points of these oxides (Table II) are higher than the appearance temperature (Table III), it is difficult to explain why the analyte oxide is in gaseous form. Normally, the melting points are obtained on bulk quantity of the oxides. In the present experimental conditions, these oxides are in an extremely small concentration distributed over a relatively large area. The analyte oxides would be deposited in the furnace in nano-layer form (15). These conditions are quite favorable to reduce the cohesive energy of the oxides and helps in the sublimation process. This indicates that in spite of the melting point being higher than T_{app} , the oxide dissociation process for these elements is favorable. On the other hand, free energy change for the reduction of the Cu and Co oxides is -ve at T_{app} ; thus, carbothermic reduction is favored for these oxides.

At appearance temperature, CuO and CoO are in solid form as their melting points are higher than T_{app} . In case of Cu, two E_a values were obtained indicating two different processes prior to atomization. The activation energy of 78 kcal/mol at appearance temperature (1208 K)

corresponds to the heat of sublimation of $Cu_{(s)(m.p.1356K)}$ after the carbon reduction of the copper oxide. Above 1320 K, the E_a value of 46 kcal/mol was observed which corresponds to a Cu-Cu bond dissociation energy in the Cu dimer. Formation of dimers and other metal clusters is well established (16). Dimer formation at higher temperatures is possible due to increased atom density. In case of Co, only a single E_a value was observed, which agrees well with the sublimation of Co, suggesting that the precursor to the free Co atom is $Co_{(s)}$.

Atomization From Zr Matrix

The activation energies for the elements Cd, Co, Cu, Mn, and Zn in the zirconium matrix were nearly the same as in the aqueous solution. In contrast to aqueous solutions, single activation energy (85 kcal/mol) was obtained for Cu. E_a agrees with the sublimation of $Cu_{(s)}$ after the carbothermic reduction. For comparison, the Arrhenius plots for Cu in the aqueous, as well as in the Zr matrix, are shown in Figure 3. In the Zr matrix, at higher temperatures, the dimer is not formed, probably free atoms are physically trapped in the high matrix concentration, and atom density is reduced, which restricts the formation of dimer. Hence, the basic mechanism remained the

same. In all cases, only the atomization efficiency is affected in the presence of the matrix and not the mode of atomization. The signal appearance temperature in the Zr matrix was found to increase. An increase in T_{app} in Zr, compared to aqueous solution, can be due to the slow release of the analytes from the high matrix concentration. In the presence of the matrix, oxygen concentration (oxygen release) (17) in the system increases due to matrix decomposition, which slows down the oxide dissociation as well as the carbothermic reduction processes, thereby shifting the appearance of the absorbance signal to a higher temperature.

Analytical Procedure

Based on these studies, analytical procedures were developed for the direct determination of Cd, Cu, Co, Mn, and Zn in the presence of Zr (10 mg/mL) matrix. Working curves obtained in the aqueous and the Zr matrix, for Mn as a model element, are shown in Figure 4. This figure indicates that the sensitivity is reduced in the Zr matrix. The optimized experimental parameters, linear analytical range, lowest absolute amount determined, and the sensitivities calculated for all of the elements in this study are listed in Table IV. Sensitivity is the change in absorbance with unit

TABLE III
 T_{app} and E_a Values in Aqueous and Zr Matrices
With Reaction Intermediates

Element	Signal Appearance Temperature (K)			Activation Energy (kcal/mole)			Reaction Mechanism in Aqueous Solution
	Aqu. ^R	Aqu.	Zr	Aqu. ^R	Aqu.	Zr	
Cd	720	910	1181	65	62	64	$CdO_{(s)} \rightarrow CdO_{(g)}$; $CdO_{(g)} \rightarrow Cd_{(g)} + 0.5 O_2$
Co	1440	1750	1900	97	106	112	$CoO_{(s)} + C \rightarrow Co_{(s)} + CO$; $Co_{(s)} \rightarrow Co_{(g)}$
Cu	1270	1270	1497	81/47	78*/46**	85	$CuO_{(s)} + C \rightarrow Cu_{(s)} + CO$, (i) $Cu_{(s)} \rightarrow Cu_{(g)}$ Lower Temp. (ii) $Cu_{2(g)} \rightarrow Cu_{(g)}$ Higher Temp.
Mn	1480	1600	1804	96	101	106	$MnO_{(s)} \rightarrow MnO_{(g)}$; $MnO_{(g)} \rightarrow Mn_{(g)} + 0.5 O_2$
Zn	1140	1200	1240	65	64	64	$ZnO_{(s)} \rightarrow ZnO_{(g)}$; $ZnO_{(g)} \rightarrow Zn_{(g)} + 0.5 O_2$

^R = Reported (13); *Lower temperature; ** Higher temperature.

change in concentration. It is calculated from the slope of the analytical plot. The lowest amount determined for these elements in aqueous solution (in $\mu\text{g/mL}$) was Cd:0.0002; Co:0.005; Cu:0.002; Mn:0.01; and Zn:1.0; and in the Zr matrix (in ppm) it was Cd:0.05; Co:0.5; Cu:1.0; and Mn:1.0, and Zn:

5 (213.9 nm) and 100 (307.6 nm). The lowest amount determined in ppm is based on the matrix concentration, which in the present case was 50 $\mu\text{g Zr/aliquot}$. In spite of the high pre-atomization losses, it was possible to determine Cd and Zn at pictogram and nanogram levels, respectively.

Since the Zn 213.9 nm analytical line is highly sensitive, a water blank also contributes to the absorbance signal; hence, for aqueous solutions, 307.6 nm, a less sensitive analytical line is preferred. In the Zr matrix, the sensitivity is reduced due to analyte entrapment, and thus it was possible to use the

Fig. 3. Arrhenius plots for Cu in (a) aqueous and (b) Zr matrix.

Fig. 4. Analytical plot for Mn in aqueous and Zr matrix.

TABLE IV
Analytical Results

Anal. Line (nm)	Matrix	Ash/Atomic Temp. (K)	Analytical Range		Absolute Amount Determined (g)	Sensitivity	Regression
			($\mu\text{g/mL}$)	(ppm)		Abs/ $\mu\text{g mL}^{-1}$	
Cd 228.8 nm	Aqu.	573/2173	0.0002-0.01	-	1.0×10^{-12}	84.7	0.99296
	Zr	873/2473	0.0005-0.01	0.05-1	2.5×10^{-12}	11.73	0.99855
Co 240.7 nm	Aqu.	573/2773	0.005-0.1	-	2.5×10^{-11}	6.25	0.9984
	Zr	873/2873	0.005-0.15	0.5-15	2.5×10^{-11}	4.08	0.994980
Cu 324.7 nm	Aqu.	573/2573	0.002-0.05	-	1.0×10^{-11}	15.1	0.99774
	Zr	873/2673	0.01-0.15	1.0-15	5.0×10^{-11}	5.51	0.99565
Mn 404.4 nm*	Aqu.	573/2673	0.01-0.2	-	5.0×10^{-11}	5.39	0.99242
	Zr	873/2723	0.01-0.5	1.0-50	5.0×10^{-11}	1.78	0.99772
Zn 307.6 nm*	Aqu.	573/2073	1.0-50	-	5.0×10^{-9}	0.029	0.99804
Zn 307.6 nm	Zr	873/2173	1.0-20.0	100-2000	5×10^{-9}	0.014	0.99916
	Zr	873/2173	0.05-0.5	5-50	2.5×10^{-10}	2.72	0.99948

*Less sensitive analytical line.

most sensitive (213.9 nm) analytical line. The analytical plots for Zn in the Zr matrix are shown in Figure 5 with both analytical lines. Using the 213.9 nm analytical line, Zn can be determined as low as 5 ppm in the Zr matrix compared to 100 ppm with the 307.6 nm line.

In the present studies, the Zr solution contains both nitrate and fluoride ions. In view of this, the performance of the methods was checked by analyzing two synthetic samples for each of the analytes in HNO_3 and in HNO_3 +HF mixture. The samples were prepared from high purity elemental solutions (E. Merck, Darmstadt, Germany) and analyzed against standards prepared in nitrate medium where no HF was used. The results are listed in Table V. The amounts estimated in nitrate solution, as well as in a $\text{HF}+\text{HNO}_3$ mixture for the same concentration of the analytes, were in good agreement with the added amounts. The results indicated that there is no interference due to fluoride ions present in the Zr matrix. Precision of the determination was found to be 10% RSD. Thus, the method proposed can successfully be utilized for the determination of the elements Cd, Co, Cu, Mn, and

Zn in 10 mg/mL of Zr matrix. However, standard/sample matching is essential with respect to matrix concentration.

CONCLUSION

Analytical methods were developed for the determination of Cd, Co, Cu, Mn, and Zn in a Zr matrix without prior chemical separation of Zr, and the effect of Zr matrix on their determination was studied. The presence of Zr reduces the absorbance significantly. Reduction in the absorbance could be due to physical trapping of the analyte in the high matrix concentration. An accumulation of matrix inside the furnace did not have a significant effect on the absorbance signal. From the atomization mechanism it was observed that the basic atomization mechanism does not change in a Zr matrix. In case of Cd, Mn, and Zn, free atoms are formed by gaseous metal oxide dissociation, while Cu and Co undergo carbothermic reduction of the metal oxides, followed by sublimation of the metal. The absence of a high temperature dimer for Cu in the Zr matrix was due to physical trapping of the atoms in a high matrix concentration which reduces the atom den-

sity and restricts the formation of dimer. In all cases, only the atomization efficiency is affected in the presence of the matrix, not the mode of atomization. In spite of the reduction in absorbance signal in the Zr matrix, these elements can be determined at significantly low concentrations. The lowest amounts determined for all of the analytes in the Zr matrix in ppm are Cd:0.05, Cu:1.0, Co:0.5, Mn:1.0, and Zn:5.0 and 100. Using the 213.9 nm analytical line, Zn can be determined as low as 5 ppm in the Zr matrix compared to 100 ppm at the 307.6 nm line. The reproducibility of the determination was 10% RSD for all of the analytes. The method developed here is suitable for the direct determination of Cd, Co, Cu, Mn, and Zn in a Zr matrix. However, due to a matrix suppression effect, prior knowledge of the sample with respect to matrix is essential.

Fig. 5. Analytical plots for the Zn 213.9 and 307.6 nm lines.

TABLE V
Analysis Results for the Samples
in HNO_3 and HNO_3 +HF Mixture

Element	Amount Added ($\mu\text{g/mL}$)	Amount Estimated ($\mu\text{g/mL}$)	
		HNO_3	HNO_3 +HF
Cd	0.001	0.001	0.001
	0.005	0.0049	0.0048
Co	0.010	0.0098	0.0098
	0.020	0.0201	0.020
Cu	0.020	0.0195	0.0199
	0.050	0.049	0.045
Mn	0.050	0.0498	0.503
	0.150	0.153	0.156
Zn	5.000	5.01	5.17
	10.00	11.8	9.38

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