Energy Dispersive X-Ray Fluorescence Determination of Gallium in Aqueous Uranium Solution and (U-Ga) Mixed Oxide Powders

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INTRODUCTION

Gallium (Ga) compounds such as GaN and GaAs are used as semiconductors, especially in light-emitting diodes, while the new photovoltaic compound Cu(In,Ga)(Se,S)_2 is reported to be useful in solar panels as an alternative to crystalline silicon (1). Since Ga readily alloys with most metals, it is used as a component in low-melting alloys. In particular, it helps to stabilize the allotropes of plutonium. Ga-U and Ga-Pu systems have been studied for the development of new metal fuel reactors with respect to their thermodynamic stability for high temperature applications (2). Gallium is known to degrade the properties of many metallic materials via corrosion, embrittlement, or intermetallic phase formation. Thus, sensitive and reliable methods for the determination of trace and minor concentrations of Ga are required in these types of materials.

For the determination of trace amounts of Ga, analytical techniques such as atomic absorption spectrometry (3), neutron activation analysis (4), and atomic emission spectrometry (AES) (5) are being used. While neutron activation methods are applicable to sub- μg levels, the detection limits for methods based on molecular absorption or fluorescence are higher (6,7). Determinations using inductively coupled plasma optical emission spectrometry (ICP-OES) (6), inductively coupled plasma mass spectrometry (ICP-MS) (7),

ABSTRACT

Energy dispersive X-ray fluorescence (EDXRF)-based methods were developed for the determination of gallium (Ga) in aqueous solution using a set of standard solutions in the concentration range of 20-5000 $\mu\text{g/mL}$. When these methods were applied to the determination of Ga in U-containing solutions, the estimated values were found to be lower due to matrix effects. Hence, they were modified using another set of Ga standards containing U concentrations at 100 mg/mL . The modified method was found to be applicable for the estimation of Ga from 50 $\mu\text{g/mL}$ to 5 mg/mL (i.e., 0.005% to 0.5% Ga in U).

Synthetic samples were analyzed by these methods in order to evaluate their reliability and reproducibility. Another method was also developed for the direct determination of Ga in (U-Ga) mixed oxide powders in the concentration range of 0.02 to 50 mg/g . The developed methods will be especially useful for the fast routine determination of Ga in U-Ga alloys.

and fluorimetry (8,9) involve separation of interfering ions. Electrochemical techniques are reported to be good and sensitive for the determination of Ga at the 10 $\mu\text{g/mL}$ level (10). Laser-induced breakdown spectroscopy has also been used for the determination of Ga in liquid matrices (11). These techniques, though sensitive, are time-consuming and have disadvantages such as the need for dissolution, chemical pre-concentration, separation treatment of the samples, and other

manipulations. Total X-ray reflection spectrometry (TXRF) is reported to be very sensitive for many trace elements with detection limits in the order of 0.1 ng/mL . However, Ga is usually used as the internal standard in the TXRF technique.

Energy dispersive X-ray fluorescence (EDXRF) spectrometry is known to be a simple, fast, non-destructive technique with adequate sensitivity (10-50 $\mu\text{g/mL}$) for many elements (12). In particular, this technique is expected to be useful for the determination of Ga (1000-10,000 $\mu\text{g/g}$) in U/Pu alloys after sample dissolution.

In the present work, feasibility studies were carried out for the determination of Ga in aqueous uranium solutions. This was done by establishing an EDXRF method for the analysis of dissolved U-Ga alloy samples. In our laboratory, (U-Ga) alloy samples are normally converted into oxide form for the determination of common metallic impurities by carrier distillation-based DC arc-atomic emission spectrometry. For this reason, a method for the direct determination of Ga in a (U-Ga) oxide mixture in powder form was also developed. The effect of common impurities in the determination of Ga in a (U-Ga) oxide mixture was examined. Electrothermal atomic absorption spectrometric (ETAAS) measurements were done using a modular type Varian Techtron AA-6 AAS equipped with a pyrolytically coated carbon rod atomizer (Varian Inc., USA), while ICP-OES measurements were done using a Jobin-Yvon axial ICP-OES spectrometer (Jobin Yvon Inc., France).

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EXPERIMENTAL

Instrumentation

The EDXRF measurements were carried out with a Jordan Valley EX 3600-M spectrometer, equipped with an Rh anode X-ray tube, an assembly of six filters, a Ge secondary target and Si(Li) detector (1–40 keV) in air (Jordan Valley Co., USA). The system software (nEXt) for spectra acquisition and analysis runs were performed using the Windows® NT 4.0 or higher operating system. The Si(Li) detector has a resolution of 139 eV at Mn-K α (5.9 keV) and is capable of acquiring a spectrum in the 1–40 keV energy region. The data acquired were processed with the help of an attached computer. The resulting intensity is expressed in counts per second (cps).

Standard Solutions

Two sets of synthetic Ga standard solutions in the concentration range of 20 to 5 mg/mL were prepared. The first set contained only Ga, while the second set contained varying concentrations of Ga (20 to 5 mg/mL) and a fixed concentration of U (100 mg/mL). About 8 mL each of the above solutions was transferred into special plastic cups (25 mm dia.) with a thin Mylar® film (thickness of 6.3 μ) at the bottom for EDXRF analysis.

Two synthetic samples were prepared and analyzed by the proposed EDXRF method and also by graphite furnace AAS (GFAAS). One synthetic aqueous standard each was analyzed by EDXRF, ETAAS, and ICP-OES for comparison purposes. One set of aqueous solutions with a fixed Ga concentration and varying amounts of U (1–100 mg/mL) was prepared to examine the matrix effects, i.e., the interference from U on the determination of Ga.

For the determination of Ga in (U-Ga) mixed oxides, the samples in the form of powder (200 mg)

were kept inside a Teflon® cup assembly, covered at the bottom with a thin Mylar film. A series of synthetic powder standards with Ga concentrations ranging from 0.02–5.0% were prepared by mixing and grinding stoichiometric amounts of high purity U₃O₈ and Ga₂O₃. Grinding was done for 30 minutes using pestle and mortar.

The optimum parameters for the determination of Ga were obtained by varying the X-ray tube current, voltage, and counting times and using the standard containing 5% Ga. All measurements were performed in air. Three synthetic (U-Ga) oxide samples were prepared for counter-checking the method. In addition, three other (U-Ga) oxide samples containing 100, 500, and 1000 μ g/g, respectively, of some common impurities such as Ca, V, Fe, Cr, Mn, Cu, Ni, Co, Zn (along with 10 mg/g of Ga) were also analyzed by the developed method.

RESULTS AND DISCUSSION

Aqueous Solutions

The standard with the highest concentration of Ga was used for optimizing the experimental parameters. The X-ray tube current and voltage was varied using different filters (method 1 with a Cu filter

and method 2 with a Mo filter) to obtain maximum count rates with a high signal-to-back-ground ratio. Table I lists the results of both methods in which eight synthetic standard solutions were counted under identical conditions in triplicate. Using a linear calibration program, calibration plots were obtained using a Cu filter (background at the Ga K α X-ray peak is reduced due to CuK X-ray absorption) as well as a Mo filter (background around Ga X-ray is less since it is far away from the MoK edge). The calibration plots obtained for Ga in aqueous solutions using methods 1 and 2 are shown in Figure 1. The precision of the determinations was better than 2%, while the limit of

TABLE I
Optimum Parameters for Ga Determination in Aqueous Solution Using K α X-Rays

Method. No.	Filter Used	Optimum Parameters	Conc. Range (μ g/mL)
1.	Cu filter	25 kV, 200 μ A, 180 s, air	20–5000
2.	Mo filter	30 kV, 350 μ A, 180 s, air	50–5000

Fig. 1. Calibration plots for Ga determination in aqueous solutions.

quantification using a Cu and Mo filter was 15 and 35 $\mu\text{g/mL}$, respectively. For the Ga determination up to 1 mg/mL, the Cu filter method is better than the Mo filter method. This is due to the reduced Compton background for Ga in the presence of the Cu filter (K edge: 9.0 eV).

The effect of varying the concentrations of U on a fixed concentration of Ga (200 $\mu\text{g/mL}$) was studied by monitoring the intensities of Ga $K\alpha$ X-rays using methods 1 and 2. The results are listed in Table II. As shown in Figure 2, the decrease in Ga $K\alpha$ X-ray intensity with the concentration of U is nearly exponential, indicating that the absorption of Ga X-rays by U is the main rea-

son. Reduction of the Ga signal intensity was found to be minimum for U concentrations at 1 mg/mL (6%), while it was maximum for U concentrations at 100 mg/mL (65%). Hence, separate optimizations of the X-ray tube parameters (Table III) and calibration plots (Figure 3) were established using a second set of standards containing U at a constant concentration of 100 mg/mL for the determination of Ga. It may be noted that a lower tube current and voltage was used when the Mo filter method was used for the determination of Ga in the presence of U than for the determination of Ga in aqueous solutions. This was primarily done

in order to reduce the high count rates from uranium X-rays, which leads to increased dead time of the detector.

The analysis results of the three synthetic samples containing either Ga or Ga and U by the proposed EDXRF methods are listed in Table IV. The agreement between the determined and added concentration values of Ga for the three samples was good (within $\pm 2\%$). In order to counter-check the developed methods, the Ga concentrations in the samples were also determined using the ETAAS method, and the results are included in Table IV. The agreement between the EDXRF and ETAAS values was

TABLE II
Effect of U on the Intensity of Ga (conc. -200 $\mu\text{g/mL}$) $K\alpha$ X-Rays

U conc. ($\mu\text{g/mL}$)	I(cps)/Estimated Conc. ($\mu\text{g/mL}$) (Cu Filter Method)	I(cps)/Estimated Conc. ($\mu\text{g/mL}$) (Mo Filter Method)
0	53.4 /221	34.4 /230
1	48.3 /189	25.9 /194
5	48.0 /183	25.7 /188
10	46.2 / 162	22.2 /162
20	44.4 / 142	18.9 /135
50	39.6 / 104	14.2 / 107
100	37.4 / 65	10.2 / 61

TABLE III
Methods for Ga Determination in U-Containing Solutions Using its $K\alpha$ X-Rays

Sample No.	Method	Optimum Parameters	Conc. Range ($\mu\text{g/mL}$)
1.	Cu Filter	30 kV, 200 μA , 180 s, air	20-5000
2.	Mo Filter	25 kV, 250 μA , 180 s., air	50-5000

Fig. 2. Effect of U concentration on Ga $K\alpha$ X-ray intensity.

Fig.3. Calibration plots for Ga determination in U (100 mg/mL) containing solutions.

reasonably good (within $\pm 5\%$). In general, the precision of the Ga determination by EDXRF was better than 3% RSD down to 100 $\mu\text{g/mL}$. Below 100 $\mu\text{g/mL}$ of Ga, the precision was between ± 5 –10%. One synthetic Ga standard (concentration of 100 $\mu\text{g/mL}$) was analyzed in quadruplicate by EDXRF, ETAAS, and ICP-OES. The determined concentration values were 94 ± 3 $\mu\text{g/mL}$, 101 ± 1 $\mu\text{g/mL}$, and 108 ± 2 $\mu\text{g/mL}$, respectively. This also demonstrated the utility of the developed methods.

(U-Ga) Oxide Powders

The optimum parameters for the determination of Ga in (U-Ga) oxide powder were determined by counting the different standards with different filters, tube voltages, and currents, and are listed in Table V. It should be noted that the optimum parameters were changed for the determination of Ga at the mg/g level.

The calibration plot of the Ga $K\alpha$ X-ray intensity against its concentration was linear in the concentration range of 20–5000 $\mu\text{g/g}$ (Figure 4), indicating the absence of significant matrix effects in this range. However, Figure 5 shows

that in the concentration range of 5 mg/g (0.5%) to 50 mg/g (5%), the plot was non-linear. The intensity of Ga X-rays increased more at higher Ga concentrations. This is attributed to the significant change (reduction) in effective Z of the matrix, resulting in reduced matrix absorption and enhanced intensity of the Ga X-rays.

Three synthetic (U-Ga) oxide samples were prepared and analyzed by the developed EDXRF method. The agreement between the added and determined values was good. The precision of the determinations varied between 0.5–5.0% (see Table VI).

TABLE IV
Analysis of Aqueous Ga Samples Using EDXRF and ETAAS

Sample 1 (Added Ga 3000 $\mu\text{g/mL}$)		Sample 2 (Added Ga 1000 $\mu\text{g/mL}$)		Sample 3 (Added Ga 100 $\mu\text{g/mL}$)	
Determined ($\mu\text{g/mL}$) EDXRF	ETAAS	Determined ($\mu\text{g/mL}$) EDXRF	ETAAS	Determined ($\mu\text{g/mL}$) EDXRF	ETAAS
3006 ± 6^a	3125 ± 120^c	1032 ± 10^a	981 ± 30^c	103 ± 2^a	101 ± 5^c
3019 ± 8^b		1020 ± 6^b		99 ± 2^b	

^a Cu filter method.

^b Mo filter method.

^c ETAAS (samples were diluted by 100–1000 times and hence the precision was poorer).

Number of determinations = 4.

TABLE V
Optimized Parameters for Ga Determination in (Ga-U) Oxide Powder Mixture

Sample No.	Method	Optimum Parameters	Conc. Range
1.	Mo Filter	25 kV, 250 μA , 180 s, air	20–5000 $\mu\text{g/g}$
2.	Mo Filter	25 kV, 500 μA , 180 s., air	1–50 mg/g

Fig. 4. Calibration for Ga in Ga-U oxide powder mixture (20 $\mu\text{g/g}$ - 5 mg/g).

Fig. 5. Calibration for Ga in Ga-U oxide mixture (1–50 mg/g).

In order to examine the effect of common impurities such as Ca, V, Fe, Cr, Mn, Cu, Ni, Co, and Zn, three (Ga-U) oxide samples containing 100, 500, and 1000 µg/g of these common impurities (along with 10 mg/g of Ga) were analyzed by the developed method. As can be seen in Table VII, the determined values were in good agreement with the added Ga concentration values, indicating tolerance of the method for common impurities.

CONCLUSION

Energy dispersive X-ray fluorescence (EDXRF) methods were developed for the fast and routine determination of Ga in aqueous/U-containing solutions over a wide concentration range (50–5000 µg/mL) with reasonable precision and accuracy, without requiring chemical separation of the major matrix. Gallium can be determined in the presence of U up to 1 mg/mL using aqueous standards. For higher concentrations of U, separate calibration standards or attenuation corrections are necessary.

In addition, an EDXRF method was developed for the direct determination of Ga in (U-Ga) mixed oxide powders over a wide concentration range with reasonable precision and accuracy. This method is fast, non-destructive, and does not involve any chemical separation or mixing with a binder. An internal standard could also be used to help with accurate quantification at higher uranium concentrations.

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TABLE VI
Determination of Ga in Some Synthetic (U-Ga)
Oxide Powder Samples in Quadruplicate

Sample 1		Sample 3		Sample 3	
Added	Determined	Added	Determined	Added	Determined
(mg/g)	(mg/g)	(mg/g)	(mg/g)	(mg/g)	(mg/g)
0.1	0.107	5	4.66	10	10.07
0.1	0.098	5	4.70	10	10.20
0.1	0.103	5	4.77	10	9.98
0.1	0.099	5	4.72	10	10.02

TABLE VII
Determination of Ga (10 mg/g) in Presence
of Some Common Impurities in Triplicate

Impurity	Determined	Impurity	Determined	Impurity	Determined
Conc.	Ga Conc.	Conc.	Ga Conc.	Conc.	Ga Conc.
(µg/g)	(mg/g)	(µg/g)	(mg/g)	(µg/g)	(mg/g)
100	10.06	500	10.45	1000	10.84
100	10.28	500	10.64	1000	10.92
100	9.97	500	10.41	1000	11.05

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**AUTHOR CORRECTIONS FOR VOLUME 34, NO. 1,
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Please note author corrections for Volume 34, No 1,
January/February 2013 issue, in article entitled:

*Determination of U, S, V, Cu, Zn, Sr, Mo, and Ce in Carbonate Rocks by
Wavelength Dispersive X-Ray Fluorescence Spectrometry and ICP-OES*
by Chancal Sarbajna et al.

pg. 31, Abstract section, middle column:

line 6, reads "Mo (10.1%, at 10 ppm)"

– but should read: Mo (10.0% at 10 ppm)

line 10, reads "Ce (5.2%, at 10 ppm)"

– but should read: U (5.2%, at 10 ppm)

pg. 35, Table III, 4th column, titled DL:

1st line, 4th column, reads "0.017"

– but should read: 0.17

2nd line, 4th column, reads "0.095"

– but should read: 0.95