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Development of anodic stripping voltammetry for determination of gallium in U–Ga alloy

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Abstract

Deposition potential, deposition time, square-wave frequency, rotation speed of the rotating disc electrode and gallium concentration have been studied in detail, for trace concentration level determination of gallium metal in U–Ga alloy by square-wave voltammetry anodic stripping analysis, in 1 M $NaClO_4 + 0.5$ M NaSCN at mercury film electrode (MFE). Optimum conditions have been found for Ga(III) determination by obtaining calibration graphs for the range $1–10 \times 10^{-7}$ M gallium. Error and standard deviation less than 1% were assessed of this method with all gallium standard solutions. The developed methodology was applied successfully as a subsidiary method for the determination of gallium content in synthetic U–Ga samples with very good precision and accuracy (under 1% error and std. dev.).

1. Introduction

Uranium is not stabilized in normal atmospheric conditions. Addition of gallium makes it stabilized at normal conditions. Generally 2% to 90% gallium is added to uranium to make U–Ga alloy. Accurate and precise estimation of gallium content is an essential requirement for chemical characterization of U–Ga alloy in nuclear field. The most widely used techniques for the determination of gallium are atomic absorption spectrometry [1–3], neutron activation analysis [4–7] and atomic emission spectrometry [8]. The utility of neutron activation methods, is restricted by instrumentation cost, long exposure times or matrix interference [1,9]. With spectrometry techniques, such as atomic or molecular absorption or fluorescence, detection limits are substantially higher [1]. Inductively coupled plasma and isotope dilution-thermal ionization mass spectrometry for gallium determination, require expensive instrumentation, reagents, long exposure times and complicated procedure [10].

Applying an electroanalytical technique for the determination of elements can provide an interesting alternative to the traditional spectroscopic methods. Electrochemical techniques offer several important advantages over the traditional techniques. First of all, the cost of instrumentation is relatively low, and second, some of these techniques, as stripping voltammetry, are highly sensitive and selective [11] used at ppm and ppb level determinations.

1 M $NaClO_4 + 0.5$ M NaSCN electrolyte at pH 2 was found to be most suitable medium for gallium

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determination by Anodic Stripping Voltammetry (ASV) during the optimization of experimental conditions for electroanalytical determination of gallium, in this laboratory. The solubility of gallium in mercury and its reversible oxidation process [11] make ASV a potentially attractive approach for low level determination of this metal. So efforts were made to develop this methodology in 1 M $NaClO_4$ + 0.5 M NaSCN mixed supporting electrolyte. Glassy carbon, a vitreous form of isotropic carbon, was preferred as a substrate for MFE due to its mechanical strength, electrochemically inertness and most smooth surface [12].

2. Experimental

2.1. Instrumentation

Electrochemical analyzer, from Micro Devices Metrohm Company, model, PG Stat-30, coupled with three-electrode voltammetric cell was employed in the present studies. Glassy carbon of 4 mm diameter polished to a mirror finish employing 0.5 and 0.05 μm alumina slurry as working, glassy carbon rod of 2.5 mm diameter as counter and saturated calomel as reference electrode were used in the voltammetric cell. All the voltammograms were automatically plotted by General Purpose Electrochemical Software.

2.2. Reagents

Gallium metal from BDH Company, dissolved in aqua-regia, fumed to dryness and after proper dilution, was used in the present studies. Sodium perchlorate and sodium thiocyanate used were of Analytical Reagent grade. Argon gas of high purity, Iolar grade-2, having less than 4 ppm oxygen was used in the experiments for degassing. All potentials referred in the text are with reference to saturated calomel electrode (SCE).

2.3. Plating, cleaning and reactivation of MFE

The glassy carbon electrode was first polished with 0.5 and 0.05 μm alumina on velvet cloth in routine experiments. Otherwise, used, after a long time or its surface was disturbed it was polished with diamond paste first, then with 0.5 and 0.05 μm alumina powder after this it was ultrasonically cleaned for 5 min. The validity of the electrode surface was checked by running a cyclic voltammogram of iron in sulphuric acid. Mercury film was plated electrochemically in-situ from a solution containing Hg(II) ions, added into the supporting electrolyte solutions and deposited on electrode surface during the analysis [12,13]. After each experiment GCE was kept at a stand-by potential of −0.3 V for 30 s to remove the mercury film from it prior to each new experiment.

2.4. Synthetic gallium samples

The synthetic gallium samples were prepared as follows: An 8.182 ± 0.001 mg/g stock solution was made by dissolving pure gallium metal in required volume of aqua-regia in a volumetric flask, which was heated at 100 °C till dryness, the residue was dissolved in 0.1 M HCl and again heated to dryness, this step was repeated 2 times for the proper fuming out of aqua-regia, the resulting residue was transferred to a 100 ml volumetric flask and made up to volume with 0.1 M HCl then fresh synthetic sample concentrations were obtained by spiking the cell with appropriate volume of this stock solution.

2.5. Synthetic U–Ga samples

Appropriate 99% pure U_2O_3 was dissolved in conc. HNO_3 giving 540.70 mg/ml U concentration. The NO^{3-} ions observed to interfere in the separation of gallium from uranium. So in 2% U–Ga samples, where Ga was determined after separation, uranium solution was transferred from NO^{3-} to Cl^- form by taking 10 ml of this solution into a 25 ml volumetric flask and heated at 100 °C till dryness, the residue was dissolved in 0.1 M HCl and again evaporated, this step was repeated two times then uranium stock solution was prepared by dissolving these residues in 3 ml (stock I) and 8 ml (stock II) 0.1 M HCl.

Synthetic gallium–uranium samples were prepared as follows:

2% Gallium: 6.1183 g stock gallium solution was transferred to an already weighted 25 ml volumetric flask and from U solution (stock I), 3.629 ml was transferred to the flask, then the weight of solution was made to 10 g with 0.1 M HCl.

10%: 7.2794 g stock gallium solution was transferred to an already weighted 25 ml volumetric flask and from U solution (stock II), 0.793 ml was transferred to mixture, the weight of solution was made to 10 g with 0.1 M HCl.

2.6. Solvent extraction experiments

The gallium solvent extraction experiments were performed as follows: known amounts of synthetic samples were transferred to a 15 ml equilibration tube, followed by 2 ml of 7 M HCl. Then equilibration tube was shaken for 5 min, after it 2 ml of isopropyl ether was added. The tube was shaken for another 5 min and allowed to stand until phase separation (~5 min). After this, 1 ml of the organic phase was transferred to pollarographic cell and the organic solvent was evaporated to dryness by heating. This was followed by the addition of supporting electrolyte solution.

2.7. Procedure

The 1 M $NaClO_4 + 0.5$ M NaSCN supporting electrolyte, referred as mixed electrolyte in text was adjusted to pH 2.0 and 15 ml was placed in a dry cell and degassed for 5 min before measurement. This solution was then spiked with the corresponding stock solution of gallium to give its desired concentration.

Gallium was preconcentrated on MFE of different thicknesses at different −1.0 to −1.5 V deposition potentials, for different times in 50–500 s range with different solution stirring rates. This was followed by a 5 s rest period prior to stripping, which was carried out from −0.95 to −0.70 V in square-wave mode of different frequencies to optimize the experimental conditions for analysis. The GCE must kept at a stand-by potential of −0.3 V for 30 s to remove the mercury film from it, prior to each new experiment due to the MFE's in-situ formation that is formed along with the deposition of gallium.

3. Results and discussion

3.1. Effect of mercury film thickness

The effect of mercury film thickness on the gallium stripping peak current was studied for various mercury film thicknesses (results not shown here). The bare GCE surface and normal mercury film thickness, generally used in analysis [14] by spiking Hg(II) solution, providing 2×10^{-4} g/l concentration of Hg(II) ions in supporting electrolyte medium could not show any stripping peak of gallium oxidation indicating no deposition of gallium because reduction of gallium is a difficult electrode process [15] due to three-electron transfer, inert pair effect and high hydration enthalpy. A thick mercury film providing 1×10^{-3} g/l concentration of Hg(II) ions in supporting electrolyte medium was found to be most suitable for analysis showing the highest stripping currents for gallium because of sufficient accumulation of Ga(III) in relatively large amount of mercury. Thicker films also again show a decrease in stripping currents, due to the competitive reduction of gallium with mercury. Gallium gets deposited in lesser amount with increasing mercury. The result for stripping currents on bare GC and MF electrodes are shown in Fig. 1.

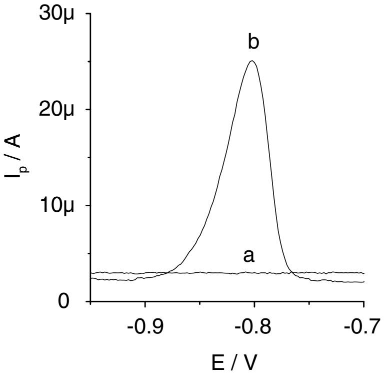

Fig. 1. Stripping currents for gallium on bare GC and MF electrodes: (a) on bare GCE surface and (b) on MFE.

3.2. Effect of deposition potential

The effect of deposition potential on gallium stripping peak current was studied, in this context first a cyclic voltammogram of 1 mM Ga(III) was run on MFE in mixed electrolyte (Fig. 2.) that shows the reduction of gallium on MFE takes place at higher −1.5 V potential. The reduction potential of Ga(III) observed from CV was enough negative for hydrogen evolution [11], so several deposition potentials in positive side to −1.5 V were studied for proper accumulation of gallium and least interference of hydrogen evolution at MFE. The effect of various deposition potentials on stripping peak current is shown in Fig. 3. The cathodic peak potential of Ga(III) reduction at MFE in mixed electrolyte medium was −1.5 V, but when the Ga(III) was deposited at −1.5 V a very small 0.92 µA stripping current could be observed because at this higher negative potential hydrogen evolves in a large amount that significantly decreases the active surface of MFE for Ga(III) reduction, the hydrogen bubbles could also be seen directly on electrode sur-

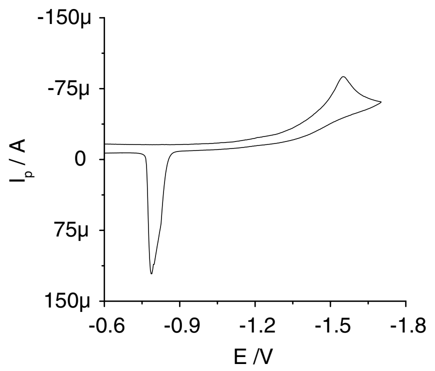

Fig. 2. CV of 1 mM Ga(III) at MFE in 1 M $NaClO_4 + 0.5$ M NaSCN, potential was cycled between −0.6 to −1.7 V at a scan rate of 50 mV/s.

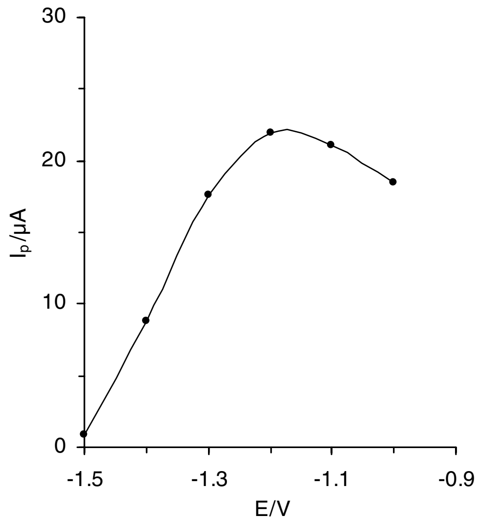

Fig. 3. Effect of different deposition potentials (−1.5, −1.4, −1.3, −1.2, −1.1 & −1.0 V) on gallium stripping currents.

face at this higher potential, after this as the deposition potential was decreased step by step to −1.2 V an increase in stripping current to 21.9 μA was observed due to the decreased hydrogen interference, on further decreasing the deposition potential to −1.0 V stripping current started to decrease to 17.2 μA because of the deposition of Ga(III) at relatively lower potentials as compare to its cathodic peak potential ($E_{pc} = -1.5$ V vs. SCE).

3.3. Effect of gallium concentration

The effect of gallium concentration on the gallium stripping current was explored for different level gallium concentrations in the range of 1–10×10^{-7} M and 1–10×10^{-6} M. For 10^{-7} M level, showing the sensitivity of this method stripping current was found to be increase from 1 to 6.7 μA, and from 4.9 to 33 μA for 10^{-6} M level with increasing gallium concentration. The slope of the Ip vs. [Ga] plot at 10^{-6} M level was found to be about 10 times greater than that at 10^{-7} M level. The gallium concentration down to 1.5×10^{-7} M could not be detected under the present experimental conditions. As errors are ever higher at low (10^{-7} M) level determination, this methodology was tried to develop at higher μM level. Results for both levels in Fig. 4 show linear dependence of stripping currents on gallium concentration, with a regression coefficient 0.99 as expected for an ideal system.

3.4. Effect of deposition time

The effect of deposition time (t_d) on gallium stripping current was explored at 5 μM gallium concentration from 50 to 500 s. However 50–350 s deposition time gallium stripping current sew a linear dependence on deposition time, but beyond 350 s gallium stripping current started to become stabilize as shown in Fig. 5.

After starting the deposition of gallium, gallium amalgam is formed in MFE that makes a shift in the rest deposition potential in negative side, so that further deposition of gallium becomes difficult with increasing time due to the increased content of insulated gallium in MFE. It becomes difficult also for Ga(III) to get reduced on MFE with time because

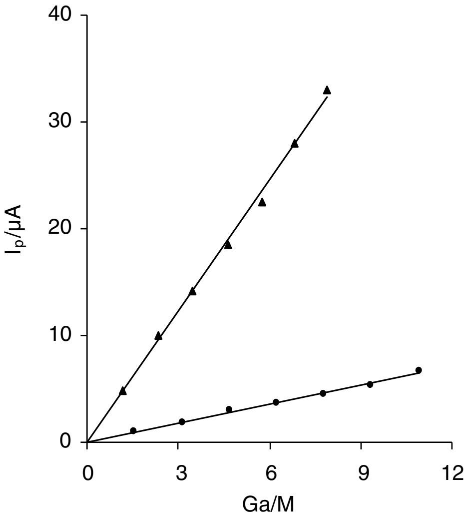

Fig. 4. Effect of gallium concentration (●) $\times 10^{-7}$ (▲) $\times 10^{-6}$ M on gallium stripping currents.

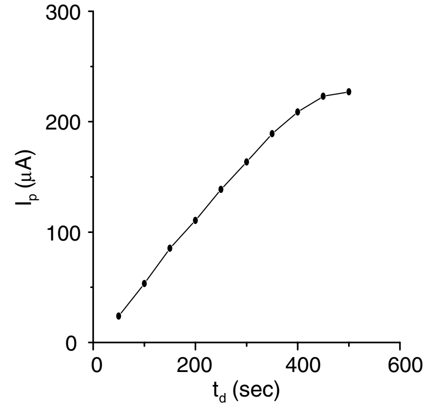

Fig. 5. Effect of deposition time from 50 to 500 s on gallium stripping currents.

at this negative potential H^+ ions also get reduced there that compete with gallium deposition, also in stripping step a certain % of whole gallium deposited during deposition step remains unstripped and this amount increases as the amount of deposited gallium is increased with deposition time [16] resulting in the curvature of plot.

3.5. Effect of rotation speed

The effect of rotation speed of electrode (N) on gallium stripping current was explored for 5 μM gallium concentration from 500 to 3000 rpm as shown in Fig. 6. The stripping current increases linearly with rotational speed of electrode. The regression coefficient found for the plot was 0.98, however, the slope of graph 0.01 μA/rpm$^{1/2}$ was very low indicating relatively small increased deposition of gallium with increasing rotation speed so there was no need practically to deposit gallium at higher rotation speeds, a 500–1000 rpm speed was suitable for the determination.

3.6. Effect of square-wave frequency

The effect of SW frequency on the gallium stripping current was explored for 5 μM gallium concentration from 20 to 120 Hz. The stripping current was found to increase from 20 to 50 μA on increasing square-wave frequency with slightly negative shift in peak potential and increased background. Results in Fig. 7 sew linear dependence of stripping currents on square root of SW frequency. Due to increased background also with stripping current, 50 Hz frequency was observed to be most suitable for analysis.

3.7. Effect of impurities/Zn

Zinc has been recognized as a potential interferent in thiocyanate-based electrolytes [17] and hinders the gallium stripping signal because zinc's redox potentials are close to gallium's redox potentials [18], due to which it also gets deposited and stripped along with gallium. Zinc remains present in supporting electrolyte and desired samples as an impurity, so it was very necessary to study its affect on determination of gallium.

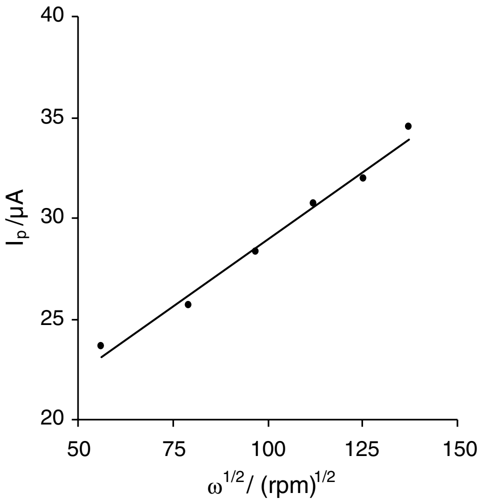

Fig. 6. Effect of rotation speed from 500 to 3000 rpm on gallium stripping currents.

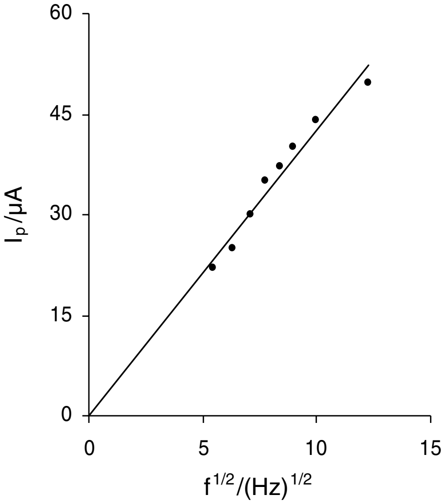

Fig. 7. Effect of square-wave frequency on gallium stripping currents.

Table 1
Determination of gallium(III) in synthetic sample solutions

Gallium amount taken (M)	No. of determinations	Mean gallium conc. detected (M)	Mean error (%)	% SD
6.18×10^{-7}	5	6.12×10^{-7}	−1.00	0.60
1.16×10^{-6}	5	1.15×10^{-6}	−0.94	0.69
2.25×10^{-6}	5	2.23×10^{-6}	−0.85	0.60
3.69×10^{-6}	5	3.66×10^{-6}	−0.88	0.86

Experiments were carried out for the determination of gallium in mixed electrolyte in the presence of 0.4 μg Zn, that was equivalent to 20 ppm as an impurity in 2% U–Ga alloy, this was much more Zn than that could be present in supporting electrolyte and desired gallium samples during the determinations. No interference of zinc on the determination of gallium was observed. Zn makes Zn–Ga intermetallic compound Zn_2Ga_3 with Ga that is the one cause of Zn interference in gallium detection at 1×10^{-7} M concentration, the stoichiometric ratio is Zn:Ga = 2:3 for the intermetallic compound, and this inermetallic compound is not observed if an excess of gallium is present [18] as in the case of our experiments where Ga was more than 10 times as compared to Zn (Zn:Ga = 1:>10) for all levels of gallium concentration as shown in Table 1.

4. Determination of gallium

After optimization of experimental conditions, developed methodology was applied for the determination of gallium in synthetic gallium as well as U–Ga samples. Gallium was preconcentrated on MFE of optimized thickness as discussed above at −1.2 V for 100 s with constant 1000 rpm solution stirring. This was followed by a 5 s rest period prior to stripping, which was carried out from −0.95 to −0.70 V in square-wave mode of 50 Hz frequency. The gallium content was determined by means of a standard addition method and GCE was kept at a stand-by potential of −0.3 V for 30 s to remove the mercury film from it prior to each new determination.

4.1. In synthetic gallium samples

The accuracy and precision of the method were assessed by analyzing synthetic samples of gallium(III) solutions in 1 M $NaClO_4$ + 0.5 M NaSCN at four different concentration levels. Single and multiple (in few determinations) addition methods were employed for the determination of gallium. Table 1 shows the results obtained. The relative mean error in all cases was exceptionally low for all concentration levels. However, the multiple standard addition method was biased to lower results.

The precession obtained at all concentration levels was under 1% SD which is very good for analysis.

Table 2
Determination of gallium in [2% (20 mg/g) and 10% (100 mg/g) gallium part] synthetic U–Ga samples

2% U–Ga samples		10% U–Ga samples	
Sample no.	Ga detected (mg/g)	Sample no.	Ga detected (mg/g)
1	19.912	6	99.825
2	19.829	7	98.916
3	19.803	8	99.098
4	19.614	9	99.405
5	19.952	10	98.326
Mean gallium conc. detected = 19.822 mg/g Mean error % = −0.90 % SD = 0.66.		Mean gallium conc. detected = 99.114 mg/g Mean error % = −0.89 % SD = 0.56.	

4.2. In synthetic U–Ga samples

The gallium content of 2% and 10% (gallium part) U–Ga synthetic samples was determined with this method. In 10% U–Ga synthetic samples gallium could be determined directly in the presence of uranium without separation of it. In 2% U–Ga synthetic samples the interference of uranium was found too much that it did not allow the proper deposition of gallium on electrode, so in these samples gallium was determined after solvent extraction from U. The solvent extraction with isopropyl ether was used, as described previously. Results in Table 2, show that this method gives very good precision and high accuracy.

5. Conclusion

Anodic Stripping Voltammetric method was developed for the determination of gallium in U–Ga alloy. Gallium content in 2% and 10% U–Ga synthetic samples could be determined with this new method with very good precision and accuracy. For U–Ga alloys where gallium is more than 10% part, gallium content can be determined directly without separation otherwise separation of gallium is required when it as less as 2% part. No interference of Zn as an impurity was observed on determination at -1.2 V. The method gives higher sensitivity, selectivity and accuracy with very good precision. In ASV determination of gallium one drawback is that gallium's reduction potential is in negative side nearer to the hydrogen evolution that limits the higher negative deposition potential.

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