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Scope of detection and determination of gallium(III) in industrial ground water by square wave anodic stripping voltammetry on bismuth film electrode

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ABSTRACT

Gallium(III) in ground water may cause human health hazards due to the antineoplastic and antimicrobial activities of gallium. However, the exposure limit of Ga(III) has not been set. This paper demonstrates the scope of employing the square wave anodic stripping voltammetry (SWASV) on bismuth film electrode (BiFE) for selective and sensitive detection of Ga(III) as well as its accurate and precise determination. The key parameters were optimized and the bismuth film morphology was characterized. The performance of BiFE was also compared with that of the mercury film electrode (MFE). The performance of BiFE was also studied for interferences of Zn(II), Cd(II), Tl(I) and Cu(II) ions. Gaussian peak fitting was performed to improve the calibration curve and the fitting process revealed almost similar stripping peak heights as obtained from the experimentally observed data though slight improvement in calibration was obtained from the peak area analysis. A good linear dynamic range (R^2 = 0.996) was obtained in the concentration range of 20–100 μg/L with a limit of detection (LOD) of 6.6 μg/L (S/N = 3) of Ga(III). A relative standard deviation of 2.9% (n = 10) was obtained for 20 μg/L of Ga(III) solution. The practical analytical utility of the method was verified by the determination of Ga(III) in spiked water samples, where 100–105% recovery of Ga(III) was achieved.

1. Introduction

Gallium (Ga) is one of the rare elements in earth crust with an average abundance of 16.9 ppm. The world production of Ga increased significantly from 16 metric tons in 1973 to 111 metric tons in 2008 due to the global urge of gallium and its compounds [1]. Gallium has no known physiologic function and it is present, most likely, in the human body due to small traces in the natural environment viz. water, vegetables and fruits. Gallium arsenide (GaAs) is one of the mostly produced gallium compounds, but it has an impact on the aquatic environment. It rapidly dissociates in water to gallium and arsenic oxides, which may further be hydrolyzed. The concentration of Ga in natural water is very low, typically less than 5 ng/L. Again, the average gallium concentrations in subsoil and topsoil are 13.8 mg/kg and 13.5 mg/kg, respectively [2]. However, due to the enormous use of gallium and gallium compounds in the industries, the ground water is being contaminated via industrial effluents. The average concentration of gallium was reported to be 19.34 μg/L and varies from 7.91 to 40.39 μg/L in the ground water in the vicinity of semiconductor industries. The average concentration of arsenic was found to be 34.81 μg/L in the same ground water [3]. The toxicity threat of gallium arsenide is generally believed to be originating from the arsenic component of this compound. However, the contribution of gallium component of this compound cannot be ignored because of the toxicopharmacology of gallium. Some of the gallium compounds have displayed anti-inflammatory and immunosuppressive activity of human disease created in test animals. Recently, gallium compounds have exhibited their potential to function as antimicrobial agents against some pathogens [4]. Therefore, the threat exists in the continuous incorporation of Ga(III) in the animal or human bodies via the contaminated ground water. Ga(III) can be easily taken up by the blood by transferrin as the transferrin–gallium complex because of the similarity between Ga(III) and Fe(III) in ionic radii and bonding characteristics. Though the exposure limit of Ga(III) has not been defined, a sensitive and reliable method is warranted for the determination of trace Ga(III) in water.

The analytical techniques developed for trace and ultra-trace determination of Ga(III) are listed in Table 1. The detection limit of spectroscopic (viz. atomic or molecular absorption, atomic emission or fluorescence) and chromatographic techniques are substantially higher. The lower limit of detection was achieved by either pre-concentration or separation step prior to the spectrometric analysis [5–12]. However, neutron activation analysis exhibits better sensitivity and lower detection limit down to the sub-μg/L level, but its utility is restricted by the instrumental cost, long exposure times or matrix interferences [13,14]. Inductively

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Table 1
Analytical techniques developed for trace and ultra-trace determination of Ga(III).

Sr. No.	Technique	Linear dynamic range	LOD	Remarks	Refs.
1.	Spectrophotometry	46.9 μg/L–2.24 mg/L	14 μg/L	Generally higher detection limits. The lower limit of detection achieved by either pre-concentration or separation step prior to the analytical step.	[5]
2.	Spectrofluorimetry	3–30 μg/L[a] 40–80 μg/L[a]	2 μg/L[a] 0.5 μg/L[a]		[6,7]
3.	Chromatography	5–100 mg/L[a]	–		[8]
4.	Atomic absorption spectrometry	0–80 ng/L[a] 0.1–0.5 mg/L	0.29 ng/L[a] –		[9–11]
5.	Atomic emission spectrometry	0.5–500 mg/L	–		[10]
6.	Neutron activation analysis	0–10 μg/L[a]	0.5 μg/L[a] 0.002 μg/L[a]	Better sensitivity and lower detection limit down to the sub-μg/L level, but utility is restricted by the	[13,14]
7.	X-ray fluorescence spectrometry	Several ppm	–	instrumental cost, long exposure times or matrix interferences	[12]
8.	ICP-MS	2–60 pM[a] 0.2–100 μg/L[a]	0.02 ppt[a] 60 ng/L[a]	Lowest limit of detection and good sensitivity for gallium, but expensive instrumentation.	[15,16]
9.	Adsorptive or anodic stripping voltammetry at mercury electrode	0.09–40 μg/L[a]	~25 ng/L[a]	The toxicity of mercury limits the use of mercury based electrodes in many countries; even use of mercury is totally banned in some of the countries.	[18–24]
10.	Voltammetry at mercury film silver based electrode	0.14-6.97 μg/L	7 ng/L		[25,26]
11.	Potentiometry at carbon nanotube composite coated platinum electrode	55.3 μg/L–2.24 g/L	36.4 μg/L	Expensive (because of carbon nanotube, platinum etc.), synthesis of ionophore is not an easy step; higher limit of detection.	[27]
12.	Present methodology	20–100 μg/L	2.3 μg/L	Simple, portable, inexpensive, selective, sensitive, rapid and accurate methodology for the determination of gallium in the ex-laboratory environments (i.e. in the vicinity of semiconductor industrial zones).	This paper

[a] Analysis was performed after a pre-concentration step or separation.

coupled plasma source mass spectrometry produces the lowest limit of detection and good sensitivity for gallium, but its expensive instrumentation may not be affordable for most of the laboratories [15,16]. Comparatively, many electroanalytical techniques are being proposed for trace or ultra-trace gallium determination because of the low instrumental cost and good sensitivity and selectivity. The standard reduction potential of Ga(III)/Ga is −0.56 V with respect to standard hydrogen electrode [17]. Thus the stripping response of gallium is masked by the hydrogen evolution current at commonly used solid electrodes like gold, platinum, silver, etc. in usual operative condition i.e. in the pH range of 1–7. Therefore, adsorptive stripping voltammetry, anodic stripping voltammetry etc. at mercury based electrodes are commonly used for the electrochemical determination of gallium [18–26]. However, the toxicity of mercury and mercury compounds used for the preparation of mercury film electrodes limits the use of mercury based electrodes in many countries; even use of mercury is totally banned in some of the countries. Therefore, considerable research emphasis has been put on the development of alternative electrode materials which would be able to deliver comparable performance as that of mercury based electrodes with low cost and possess minimal or no environmental threat.

Recently, multi-walled carbon nanotube coated platinum wire (MCNCPW) electrode was introduced as non-mercury based electrode which was employed for determination of detection of Ga(III) in the concentration range of 55.3 μg/L–2.24 g/L with a detection limit of 36.4 μg/L [27]. However the average concentration level of Ga(III) in the industrial ground water is 19.34 μg/L, which is well below the detection limit of MCNCPW electrode. Therefore, still the challenge exists to develop non-mercury based electrode for the determination of Ga(III) with much lower limit of detection. In this context, we tried to use bismuth film electrode (BiFE) introduced by Wang et al., which was shown to have a performance comparable to mercury-based electrodes [28]. The strengths and weaknesses of BiFE are recently well reviewed for its application in electroanalytical sciences [29–31]. The toxicity of bismuth and its salts is considerably lower than that of other heavy metals. Moreover, BiFE also showed some attractive properties like high sensitivity, well-defined and highly reproducible stripping signal, good resolution of neighboring peaks, low background characteristics, a large cathodic working potential range and also being insensitive to dissolved oxygen, eliminates the time-consuming de-oxygenation step. Our research group has already developed the methodology for the determination of Ga(III) in the concentration range of 70–280 μg/L by employing square wave anodic stripping voltammetry (SWASV) at *in situ* BiFE [32]. Recently, bismuth film coated on improved wax-impregnated graphite electrode showed encouraging results for ultra-trace lead and cadmium determination [33]. Therefore, the present work was mainly focused on the improvement of the same methodology for gallium determination at the average concentration level observed in the industrial ground water (i.e. ~20 μg/L) with much lower limit of detection.

SWASV is susceptible to the overlap of the gallium stripping peak with the stripping peaks of some other elements which have the standard reduction potentials in the vicinity of gallium. The standard reduction potentials of cadmium (Cd(II)/Cd), thallium (Tl(I)/Tl) and zinc (Zn(II)/Zn) are −0.402 V, −0.336 V and −0.762 V, respectively [34]. These elements can, therefore, interfere in the electrochemical determination of gallium by SWASV. Copper can interfere in a different way during the determination of gallium by BiFE. The standard reduction potential of Cu(II)/Cu (0.34 V vs. SHE) is higher than that of Bi(III)/Bi (0.32 V vs. SHE) [35]. Therefore, the competition for surface sites on the electrode surface between the deposited copper and bismuth might destroy the entire nature and performance of BiFE. However, the gallium stripping signal might be perturbed in presence of copper due to the formation of Cu–Ga intermetallic compounds [36,37]. In this context, the interference of Cu(II) in the determination of Ga(III) on BiFE was also studied in this paper.

The present paper is the first report on the possibility of trace determination of gallium in the concentration range of 20–100 μg/L by employing SWASV on BiFE in acetate buffer solution of pH 4.6. Optimization, calibration, recovery and interference studies were carried out with 20 μg/L Ga(III) concentration (i.e. the average gallium concentration in the industrial ground water). The performance of BiFE was also compared with mercury film

electrode (MFE) under the similar experimental conditions. Therefore, our methodology of SWASV at BiFE delivers a simple, inexpensive, selective, sensitive, precise and accurate determination of gallium.

2. Experimental

2.1. Chemicals and reagents

Stock solutions of 21 mg/L of Bi(III) and 271 mg/L of Hg(II) were prepared by dissolving $BiO(NO_3)\cdot H_2O$ and $HgCl_2$ (Merck, 99% purity) in 0.05 M HNO_3. The standard stock solution of 1000 μg/L of Ga(III) was prepared by dissolving high purity gallium (99.9% purity) in AR grade concentrated HCl under reflux conditions and test solutions were prepared by diluting as required. The concentration of gallium in the stock solution was also confirmed by Isotope dilution-Thermal Ionization Mass Spectrometry. Standard stock solutions of cadmium, thallium and zinc (1000 mg/L, atomic absorption standard solutions) were obtained from Merck and diluted as required. A 0.2 M sodium acetate buffer solution of pH 4.6 was used as the supporting electrolyte.

All the solutions were prepared using Millipore-Milli-Q water (18 MΩ cm^{-1}). All measurements were carried out at room temperature (25 ± 1 °C). The SWASV experiments on MFE were carried out after purging the solution with high purity nitrogen for 15 min.

Certipure standard solution of gallium nitrate in 2–3% HNO_3 (concentration of Ga(III) 1000 mg/L) was obtained from Merck and was used for recovery studies by employing our proposed methodology.

2.2. Instrumentation

All voltammetric experiments were performed with Autolab PGSTAT30 and ECD modules driven by General Purpose Electrochemical System (GPES) 4.7 software. A three-electrode configuration consisting of glassy carbon (GC) disc of 3 mm diameter working electrode, platinum rod counter electrode and Ag/AgCl (3 M NaCl) reference electrode was used in the voltammetric experiments. The GC working electrode was polished with 0.05 μM alumina slurry prior to performing each set of experiments.

The surface morphology of BiFE was recorded *ex-situ* by Nanosurf EasyScan 2 atomic force microscope (AFM) by employing tapping mode at the amplitude of 200 mV. The surface morphology of BiFE was compared with that of the bare glassy carbon electrode recorded under the same conditions. The recorded surface morphology was analyzed by inbuilt programs of the Nanosurf Report 4.1 software.

2.3. Procedure for preparation of BiFE

Bismuth film electrode was prepared on GC by depositing Bi *in situ* from 500 μg/L of Bi (III) solution in acetate buffer solution (pH 4.6) at −1.2 V for 240 s under stirring conditions (500 rpm). The deposited bismuth film was stripped off the GC electrode by

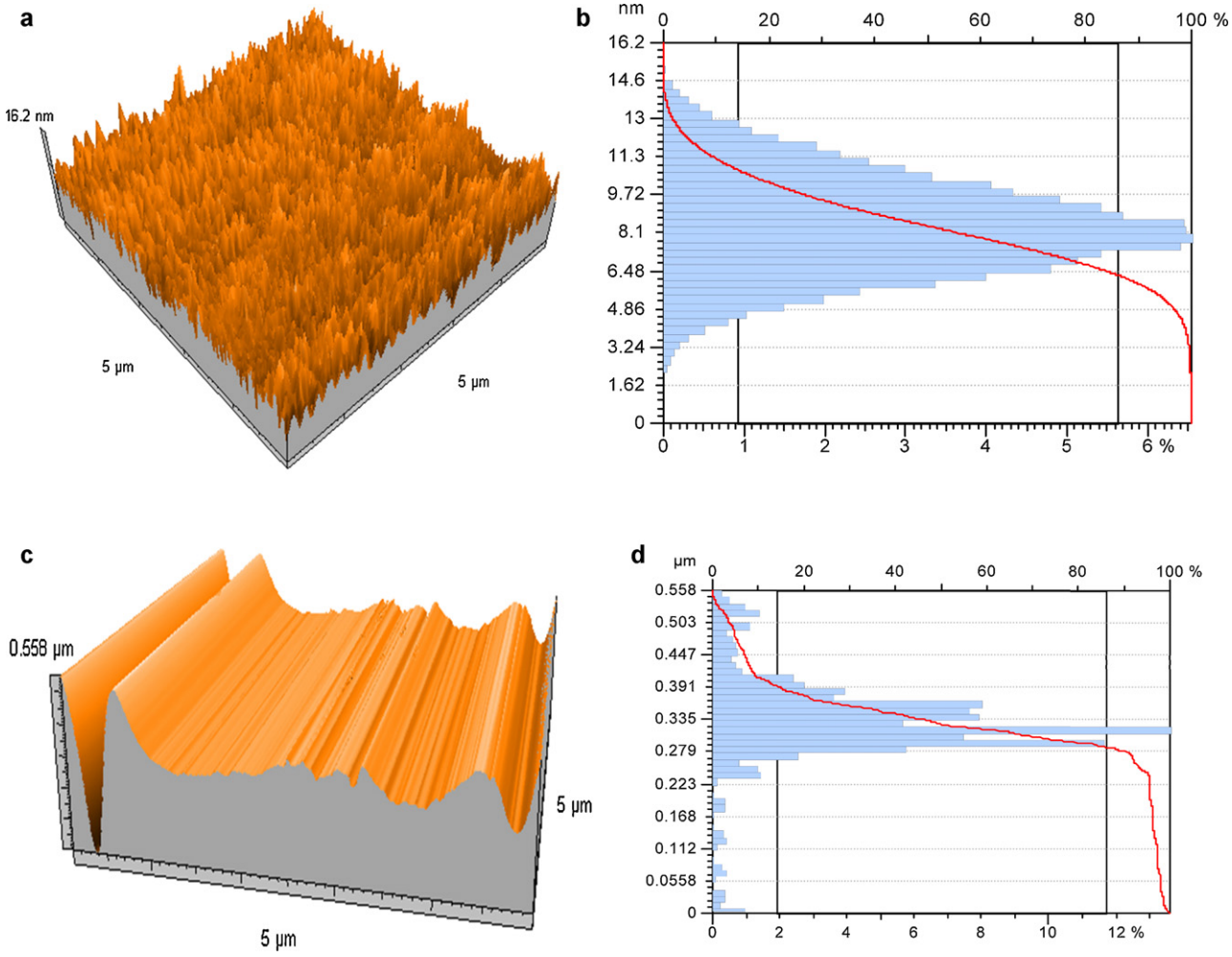

Fig. 1. Surface topographies of: (a) bare glassy carbon electrode and (c) BiFE. The height distributions of (b) bare glassy carbon electrode and (d) BiFE.

scanning the potential from −1.2 V to 0.5 V at a scan rate of 0.124 V/s. The anodic stripping peak of Bi was observed at 0.008 V (Fig. S1).

The surface morphologies of bare GC and BiFE are shown in Fig. 1. The average surface height of bare GC is ~8.1 nm (Fig. 1a and b) and average root mean square area roughness is 2.03 nm. In contrast, the BiFE appeared as non-plainer layered surface of maximum and average heights of 600 nm and 300 nm, respectively (Fig. 1c and d). The average root mean square roughness of the BiFE was observed to decrease to 0.91 nm and it indicated the existence of a smooth film of BiFE.

2.4. Procedure for preparation of MFE

Mercury film electrode was prepared on GC by depositing Hg *in situ* from 13.5 mg/L of Hg(II) solution in acetate buffer solution (pH 4.6) at −1.2 V for 240 s under stirring conditions (500 rpm). The deposited mercury film was stripped off the GC electrode by scanning the potential from −1.2 V to 0.8 V at a scan rate of 0.124 V/s. The anodic stripping peak of Hg was observed at 0.499 V (figure not shown).

3. Results and discussion

3.1. Optimization of SWASV parameters for determination of gallium on BiFE

Gallium was co-deposited with bismuth during *in situ* formation of BiFE from 40 μg/L of Ga(III) in presence of 500 μg/L of Bi(III) in acetate buffer solution at pH 4.6. The stripping peak of gallium was observed at −0.915 V while scanning the potential from −1.2 V to 0.5 V at a scan rate of 0.124 V/s (Inset of Fig. S1). Renewal of GC surface is one of the important requirements for obtaining reproducible results. Fig. S2a shows the stripping peak current of Ga (I_p^{Ga}) as a function of preconditioning time (t_c). I_p^{Ga} decreased from 4.7 μA to 3.2 μA on increasing t_c from 30 s to 120 s and it attained stable value beyond 120 s. We selected 240 s as the optimum preconditioning time for all the experiments. Preliminary investigations showed that the deposition potential (E_d), deposition time (t_d), square wave frequency (f) and square wave amplitude (ΔE) were all significant factors for reliable determination of Ga on BiFE. Thus optimization was carried out by monitoring the gallium stripping peak current as a function of these parameters.

The variation of stripping peak current of Ga (I_p^{Ga}) was studied by varying the deposition potential (E_d) from −1.0 V to −1.5 V for 240 s and the results are shown in Fig. S2b. I_p^{Ga} increased linearly on reducing E_d from −1.0 V to −1.2 V, but beyond this potential, I_p^{Ga} again decreased on further reducing E_d. As the deposition potential becomes more cathodic, more amount of material (both Ga and Bi) gets deposited on the electrode surface due to increasing rate of electrodeposition. Beyond −1.2 V, hydrogen evolution is accompanied by the deposition process and it disturbs the deposited layer and finally leads to lesser compact film. Therefore, deposition potential of −1.2 V was selected to be optimum under our experimental conditions.

The influence of deposition time (t_d) on I_p^{Ga} was studied between 60 and 400 s at the deposition potential of −1.2 V. Fig. S2c shows the variation of I_p^{Ga} as a function of t_d. It was observed that I_p^{Ga} increases with increasing t_d. The increased peak height for higher deposition time can be exploited to improve the detection limit of Ga. However, I_p^{Ga} reached a plateau above 240 s and further increase in t_d up to 400 s produced no advantage in sensitivity; thus indicating the saturation of the electrode surface. Therefore, deposition time of 240 s was fixed for subsequent studies.

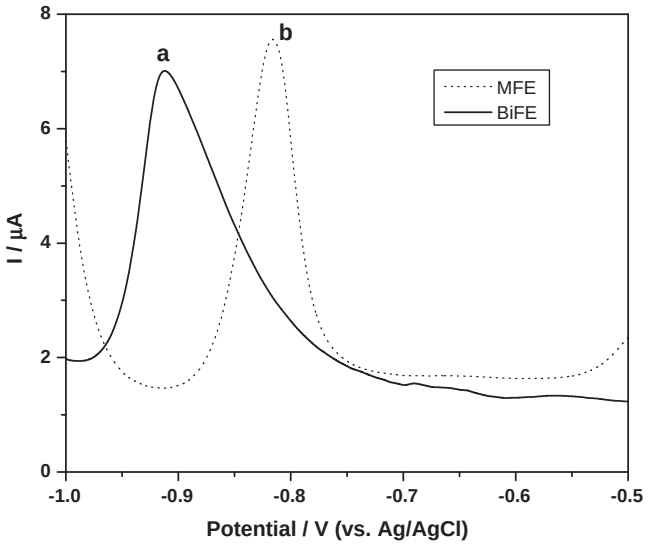

Fig. 2. SWASV 20 μg/L Ga(III) on (a) BiFE and (b) MFE in acetate buffer solution (pH 4.6). Bi(III): 500 μg/L; Hg(II): 13.5 mg/L; Ga(III): 20 μg/L; deposition potential: −1.2 V; deposition time: 240 s; square-wave frequency: 25 Hz; amplitude: 60 mV; potential step: 5 mV; stripping potential range: −1.1 to 0.5 V (for BiFE) and −1.1 to 0.8 V (for MFE).

The influence of square waveform parameters viz. amplitude (ΔE; 10–90 mV) and frequency (f; 25–60 Hz) was also studied during the SWASV of Ga on BiFE. The effect of increasing the frequency caused both the bismuth and gallium signals to increase steadily; but at higher frequencies (>25 Hz), the peaks shifted to the higher anodic potentials and simultaneously, the resolution also deteriorated because of noisy voltammograms. However, frequency of 25 Hz was sufficient to produce well resolved stripping signals. The variation of I_p^{Ga} as a function of ΔE is shown in Fig. S2d. It is seen that I_p^{Ga} increases monotonically with increasing ΔE because of the improvement in the discrimination between the faradic and non-faradic components of signal at higher values of amplitude. I_p^{Ga} attained maximum value at the square wave amplitude of 50–60 mV. However, further increase in amplitude again deteriorated the signal due to large perturbation.

3.2. Comparative study of gallium determination on BiFE and MFE

A comparative study was initially performed to ascertain whether the signal of gallium on BiFE could provide a comparable result to that obtained on MFE. The SWASV parameters viz. preconditioning time, deposition potential, deposition time, square wave frequency and square wave amplitude were fixed at 240 s, −1.2 V, 240 s, 25 Hz and 60 mV, respectively. Fig. 2 shows the SWASV of 20 μg/L of Ga(III) in acetate buffer solution at pH 4.6. The stripping peak of Ga appeared at −0.912 V and −0.816 V on BiFE and MFE, respectively. The peak height of Ga on these two electrodes is almost comparable; however BiFE produced a broader stripping peak compared to MFE. The stripping peak of Ga shifted by 96 mV towards more negative value at BiFE and this phenomenon indicates the more energetically favourable stripping of accumulated Ga from Bi–Ga alloy as compared to the same from Hg–Ga alloy. The melting points of mercury and bismuth are −38.8 °C and 271.5 °C, respectively. At ~25 °C, Ga experienced stronger interaction in mercury compared to the same in bismuth [38] and, therefore, more energy was required to strip out Ga from MFE than from BiFE.

Ten individual SWASV experiments with 20 μg/L of Ga(III) in acetate buffer solution at pH 4.6 at BiFE produced the peak potential (E_p) and peak current (I_p) of Ga at −0.912 ± 0.006 V and 6.9 ± 0.2 μA,

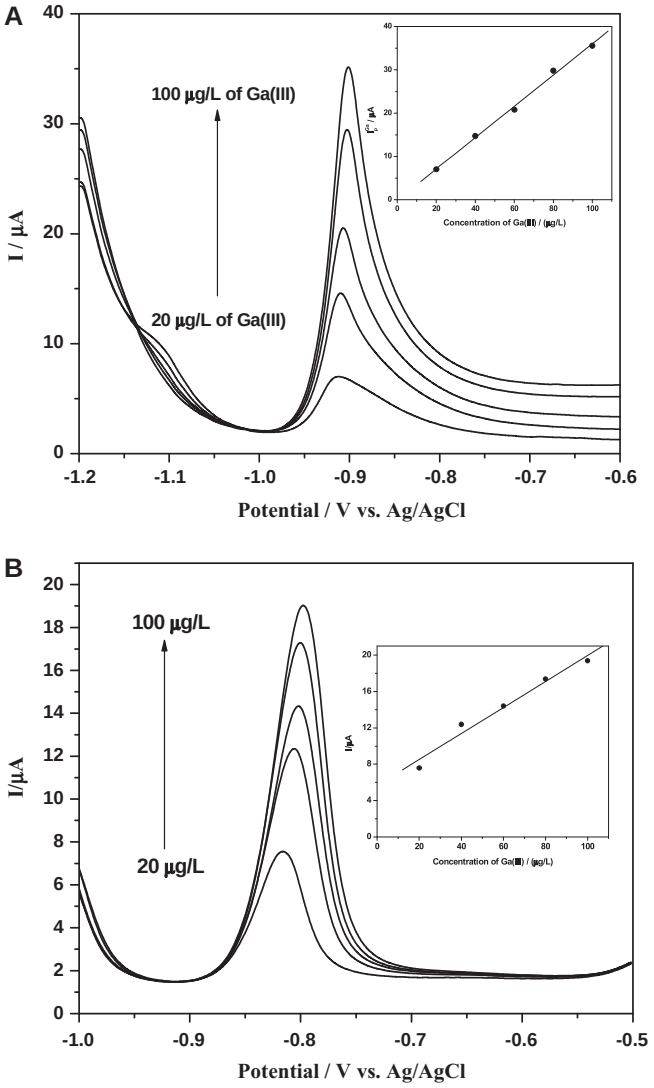

Fig. 3. SWASV for increasing concentration of Ga(III) on: (A) BiFE and (B) MFE in the concentration range between 20 and 100 µg/L in 20 µg/L steps. Insets: calibration plot of gallium over the concentration range of 20–100 µg/L. The other conditions except the stripping potential range are as in Fig. 2.

respectively. However, the same experiment at MFE produced the peak potential (E_p) and peak current (I_p) of Ga at -0.817 ± 0.008 V and 7.7 ± 0.4 µA, respectively. Calibration experiment was carried out by standard addition method in the 20–100 µg/L concentration range of Ga(III) on BiFE (Fig. 3a) and MFE (Fig. 3b) under the similar experimental conditions. The stripping peak current showed a better linear dependency ($R^2 = 0.996$) on the concentration at BiFE (Inset of Fig. 3a) compared to the linear dependency ($R^2 = 0.972$) on the concentration at MFE (Inset of Fig. 3b). The calibration equations for BiFE and MFE were obtained by least-squares regression and are expressed by Eqs. (1) and (2), respectively.

$$I_p(\mu A) = 0.361\ C(\mu g/L) - 0.086 \quad (R^2 = 0.996) \tag{1}$$

$$I_p(\mu A) = 0.143\ C(\mu g/L) + 5.664 \quad (R^2 = 0.972) \tag{2}$$

The detection limits of 6.6 µg/L and 8.0 µg/L of Ga(III) were estimated from ten replicate determinations of blank solution under optimum conditions ($S/N = 3$) [39] at BiFE and MFE, respectively.

The above results illustrate that determination of 20–100 µg/L of Ga(III) in acetate buffer solution can be performed in a better way at BiFE in non-deoxygenated analyte solutions compared to at MFE in deoxygenated analyte solutions.

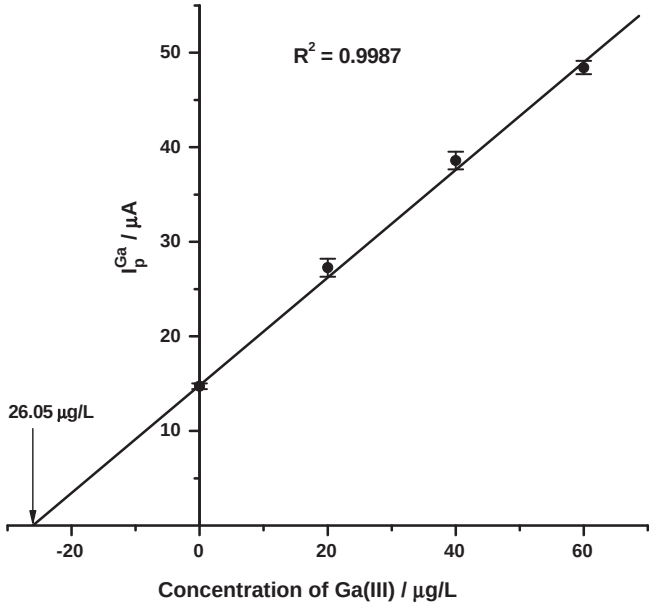

Fig. 4. Standard addition plot for determination of Ga(III) concentration on BiFE for a solution of gallium nitrate in 2–3% HNO_3. Standard addition steps: 20 µg/L of Ga(III). A set of three independent anodic stripping signals was recorded after each standard addition. The other conditions are as in Fig. 2.

Table 2
Recovery of trace Ga(III) in water by the proposed methodology.

Sr. No.	Added Ga(III) (µg/L)	Determined Ga(III) (µg/L)	Recovery (%)
1.	25.00	26.05	104
2.	25.00	26.26	105
3.	20.00	20.02	100

3.3. Recovery studies with standard gallium nitrate solution

The analytical merit of the procedure was evaluated by spiking 10 mL of acetate buffer solution (pH 4.6) with certipure standard solution of gallium nitrate in 2–3% HNO_3 (concentration of Ga(III) 1000 mg/L) obtained from Merck. This was analyzed as a certified sample (the expected amount of Ga in the sample was 250 ng) for the present purpose. Three successive standard additions of 20 µg/L Ga(III) were done to the test solution and three SWASVs were recorded after each standard addition. The mean of anodic stripping currents after each standard addition (with respective standard deviation values) were utilized for the standard addition plot as shown in Fig. 4. The recovery and precision of Ga(III) are listed in Table 2. The acceptable recovery (100–105%) indicates that the proposed method can be used for the determination of Ga(III) in water samples.

3.4. Determination of gallium in presence of cadmium, thallium, zinc and copper

In preliminary investigations on BiFE, stripping peaks of cadmium, thallium and zinc were observed at −0.770 V, −0.599 V and −1.102 V, respectively. In view of the proximity of the reduction potentials of cadmium, thallium and zinc to gallium reduction potential; we studied the interference of these metal ions on the stripping characteristics of gallium.

3.4.1. Influence of cadmium concentration on stripping peak of gallium

SWASV of gallium was carried out on BiFE in 0.2 M acetate buffer solution (pH 4.6) containing 20 µg/L Ga(III) in presence of

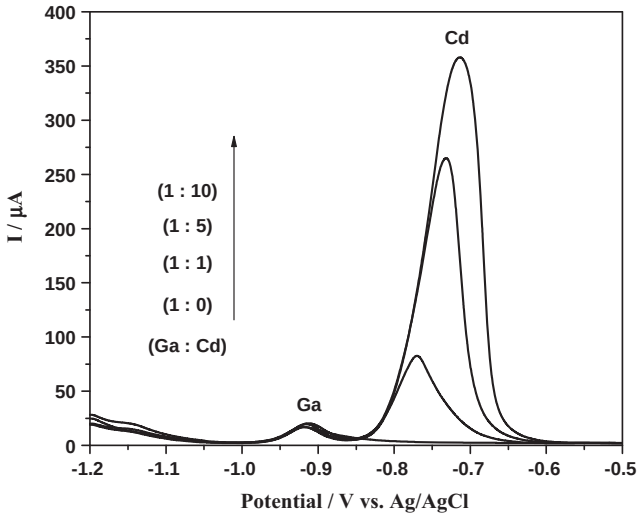

Fig. 5. SWASV of 20 µg/L Ga(III) on BiFE for increasing concentration of Cd(II) (0, 20, 100 and 200 µg/L). The other conditions are as in Fig. 2.

four different mass concentration ratios of Cd(II) (Fig. 5). The well resolved peaks of gallium (at −0.915 V) and cadmium (at −0.770 V) were observed for Ga:Cd = 1:1. The cadmium peak potential shifted by about 57 mV towards more anodic potential on increasing the Ga:Cd ratio from 1:1 to 1:10. However, well defined and well resolved gallium stripping peak could still be observed in presence of ten fold cadmium. Gallium neither forms solid solution with cadmium nor with bismuth [38]. Similarly, cadmium does not form any solid solution with bismuth [38]. Thus cadmium and gallium get deposited at BiFE independently in the form of Cd(0) and Ga(0), respectively. As a result, the stripping of gallium occurs independent of cadmium concentration. The stripping peak current of 20 µg/L gallium in 0.2 M acetate buffer solution (pH 4.6) was observed as 18.6 µA (±9.5% RSD) in presence of 20–200 µg/L of cadmium.

3.4.2. *Influence of thallium concentration on stripping peak of gallium*

SWASV study of gallium was carried out on BiFE in 0.2 M acetate buffer solution (pH 4.6) containing 20 µg/L Ga(III) in presence of four different mass concentration ratios of Tl(I) (Fig. 6a). The well resolved peaks of gallium (at −0.917 V) and thallium (at −0.599 V) were observed for Ga:Tl = 1:1. The thallium peak potential shifted by about 40 mV towards more anodic direction when increasing the Ga:Tl ratio from 1:1 to 1:4. The stripping peak current of 20 µg/L of Ga(III) in 0.2 M acetate buffer solution (pH 4.6) was observed as 12.4 µA (±5.1% RSD) in presence of 20–80 µg/L of Tl(I). Well defined and well resolved gallium stripping peak was observed in presence of four fold of thallium. However, the shape of thallium stripping peak significantly changed on increasing thallium concentration. Upto 40 µg/L of Tl(I), a single stripping peak (Tl_I) was observed at −0.599 V. For thallium concentration more than 40 µg/L, the single

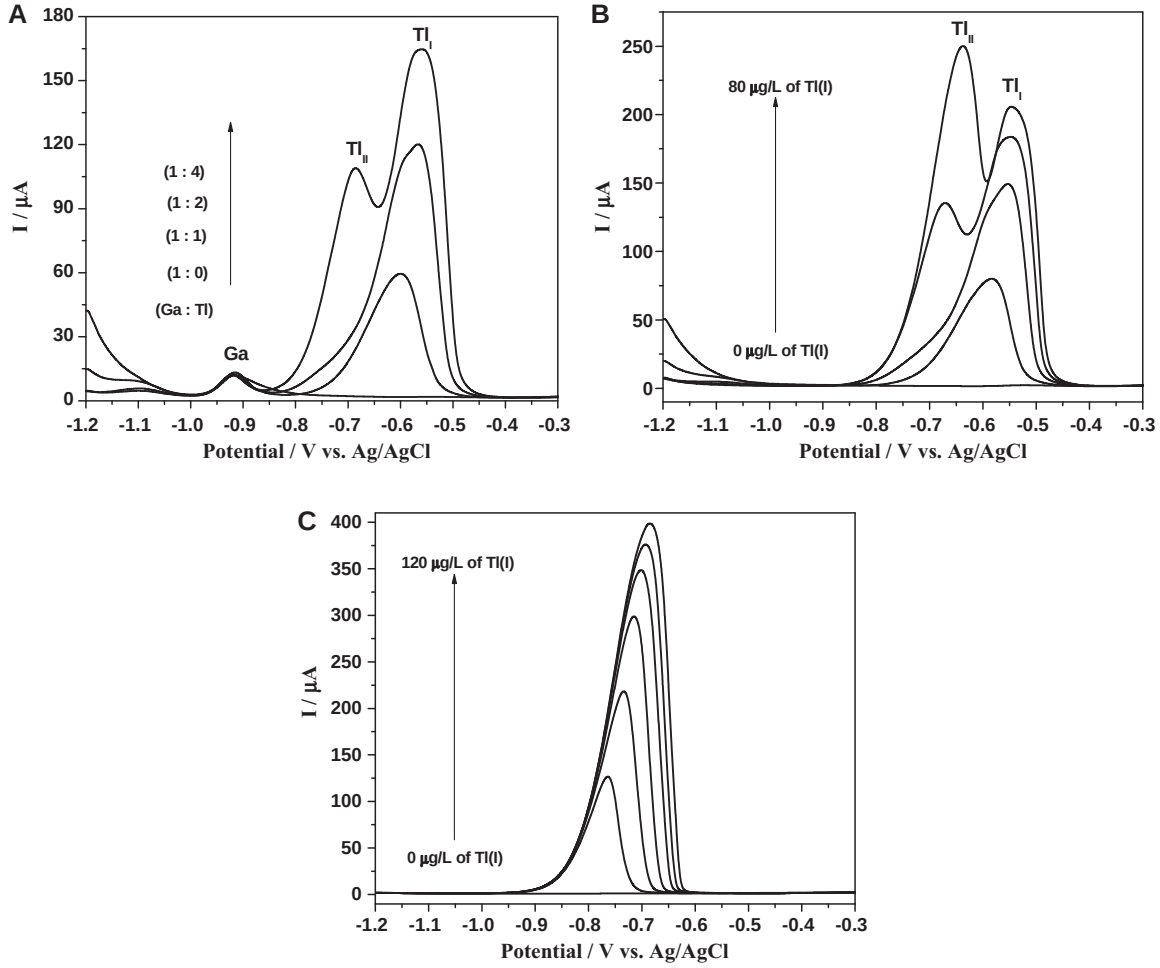

Fig. 6. (a) SWASV of 20 µg/L Ga(III) on BiFE for increasing concentration of Tl(I) (0, 20, 40 and 80 µg/L). (b) SWASV of Tl(I) on BiFE in the concentration range of 0–80 µg/L in 20 µg/L steps. (c) SWASV of Tl(I) on glassy carbon electrode in the concentration range of 0–120 µg/L in 20 µg/L steps. The other conditions are as in Fig. 2.

thallium stripping peak splitted into two peaks when the additional peak (Tl_{II}) appeared at −0.690 V. In order to investigate the origin of this additional peak at −0.690 V, we performed a similar set of experiments, in absence of gallium (Fig. 6b), when we also observed the additional stripping peak, Tl_{II}, at the same position (−0.690 V) for thallium concentration >40 μg/L. Therefore, it was ascertained that gallium is not interacting with thallium or vice versa [38]. Further, we carried out SWASV experiments with 20–120 μg/L of Tl(I) in 0.2 M acetate buffer solution (pH 4.6) on bare GC electrode in absence of Ga(III) (Fig. 6c). In this case, a well defined stripping peak of thallium was observed at about −0.7 V for the full working concentration range of thallium. The stripping peaks of thallium at −0.599 V (Tl_I) and −0.690 V (Tl_{II}) are attributed to the oxidative dissolution of thallium from the Bi–Tl intermetallics (δ-Tl) [38] and glassy carbon active surface sites, respectively.

However, electrodeposition mechanism during *in situ* formation of the bismuth film in presence of Ga(III) and Tl(I) has major influence on thallium stripping characteristic. At −1.2 V, though both gallium and thallium are co-deposited along with bismuth, but their rate of deposition differs depending on their overpotential. Therefore, a competition always exists among Ga(III), Tl(I) and Bi(III) to occupy the active surface sites on GC. Bismuth mostly occupies the active surface sites on GC because of its highest overpotential among the three elements and thus thallium and gallium get deposited on bismuth. However, due to the parallel deposition process, thallium also gets a chance to occupy some active surface sites of GC and this probability increases with increase in the concentration of thallium. Since the adherence of thallium on carbon substrate and bismuth is different, two stripping peaks of different energies appear for thallium. It is stripped off from GC sites at about −0.7 V, whereas it requires slightly more anodic potential (i.e. at −0.599 V) for stripping off from bismuth sites. Gallium has the least overpotential and thus minimum rate of deposition compared to that of thallium and bismuth. Thus gallium is significantly deposited on bismuth. Therefore, gallium does not show any effect on the stripping characteristics of thallium and vice versa.

3.4.3. *Influence of zinc concentration on stripping peak of gallium*

SWASV of gallium was carried out on BiFE in 0.2 M acetate buffer solution (pH 4.6) containing 20 μg/L Ga(III) and 20 μg/L Zn(II). In the presence of zinc, the deposition potential shows a great influence on the stripping peaks of these two elements. The stripping peak heights of both zinc and gallium increase significantly by changing the deposition potential from −1.2 V to −1.3 V (Fig. 7a). Resolution of the stripping peaks also improved at the deposition potential of −1.3 V. The well resolved peaks of gallium (at −0.917 V) and zinc (at −1.103 V) were observed for Ga:Zn = 1:1 (Fig. 7b). The gallium stripping peak was completely screened by the stripping peak of zinc on increasing the Ga:Zn ratio to 1:2.

3.4.4. *Influence of copper concentration on stripping peak of gallium*

Fig. 8A shows the effect of Cu(II) addition on the SWASV of 30 μg/L Ga(III) on BiFE in 0.2 M acetate buffer solution (pH 4.6). The anodic stripping peak of Ga(III) appeared at −0.917 V with a peak current of 30.2 μA. However, the anodic stripping peak of Ga(III) was shifted slightly towards less negative potential (at −0.912 V) upon addition of 20 μg/L Cu(II) into the solution. Also, the peak current of Ga(III) decreased significantly to 23.7 μA. Upon introducing an additional amount of 10 μg/L Cu(II) into that solution, the peak current of Ga(III) further decreased to 21.3 μA. However, no change in the peak potential was observed. Fig. 8B shows the calibration plot for Ga(III) in the concentration range of 30–50 μg/L in presence of 30 μg/L of Cu(II). The calibration equation is expressed in Eq. (3):

$$I_p(\mu A) = -0.67 + 0.735\ C(\mu g/L) \quad (R^2 = 0.999) \tag{3}$$

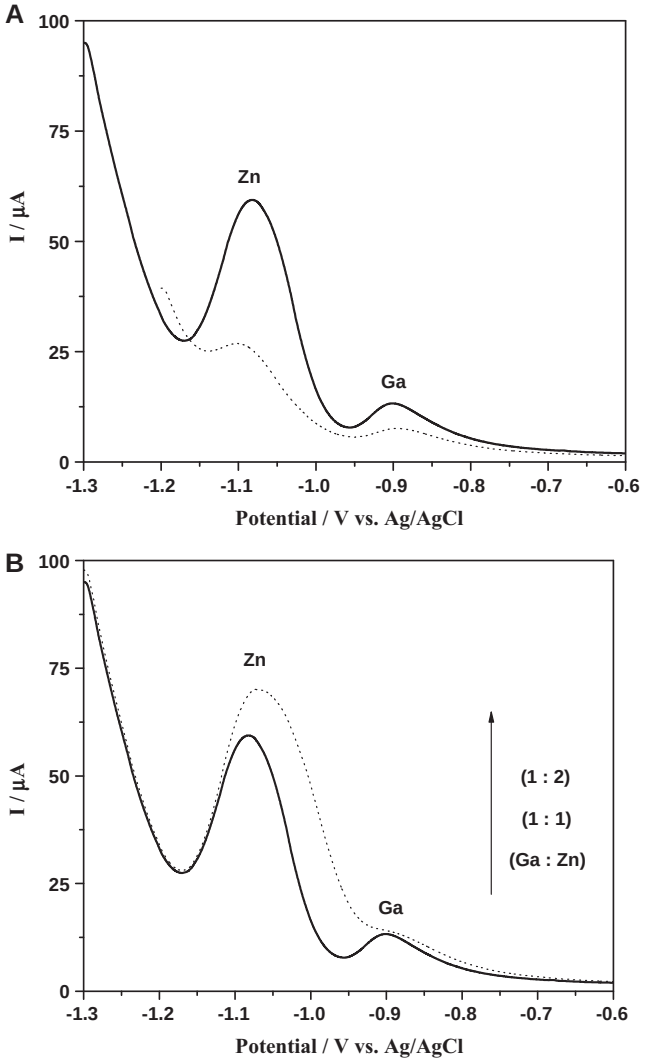

Fig. 7. (a) SWASV of 20 μg/L Ga(III) on BiFE in presence of 20 μg/L of Zn(II) at deposition potential (i) −1.2 V and (ii) −1.3 V. (b) SWASV of 20 μg/L Ga(III) on BiFE for increasing concentration of Zn(II) (20 and 40 μg/L) at the deposition potential −1.3 V. The other conditions are as in Fig. 2.

The shift in anodic stripping potential and the decrease in the stripping current of Ga(III) are observed because of the formation of gallium–copper intermetallics. This affects the sensitivity of Ga(III) concentration during the measurement. Therefore, the present methodology is not recommended in presence of Cu(II).

3.5. *Simultaneous determination of gallium in presence of cadmium, thallium and zinc using BiFE*

SWASV of gallium was carried out on BiFE in 0.2 M acetate buffer solution (pH 4.6) containing 20–140 μg/L in presence of Zn(II), Cd(II) and Tl(I) ions (20 μg/L each) at the deposition potential −1.3 V (Fig. 9a). Well resolved gallium stripping peak was observed for the entire concentration range (20–140 μg/L). The stripping peak potential (E_p) and current (I_p) for 20 μg/L Ga in presence of Zn(II), Cd(II) and Tl(I) (20 μg/L each) was observed as -0.900 ± 0.002 V and 17.8 ± 1.3 μA, respectively for ten independent SWASV experiments. Calibration experiment was carried out by standard addition method in the 20–140 μg/L concentration range of Ga(III) (Fig. 9b). The stripping peak current showed a second order polynomial dependency on the gallium concentration. The calibration equation

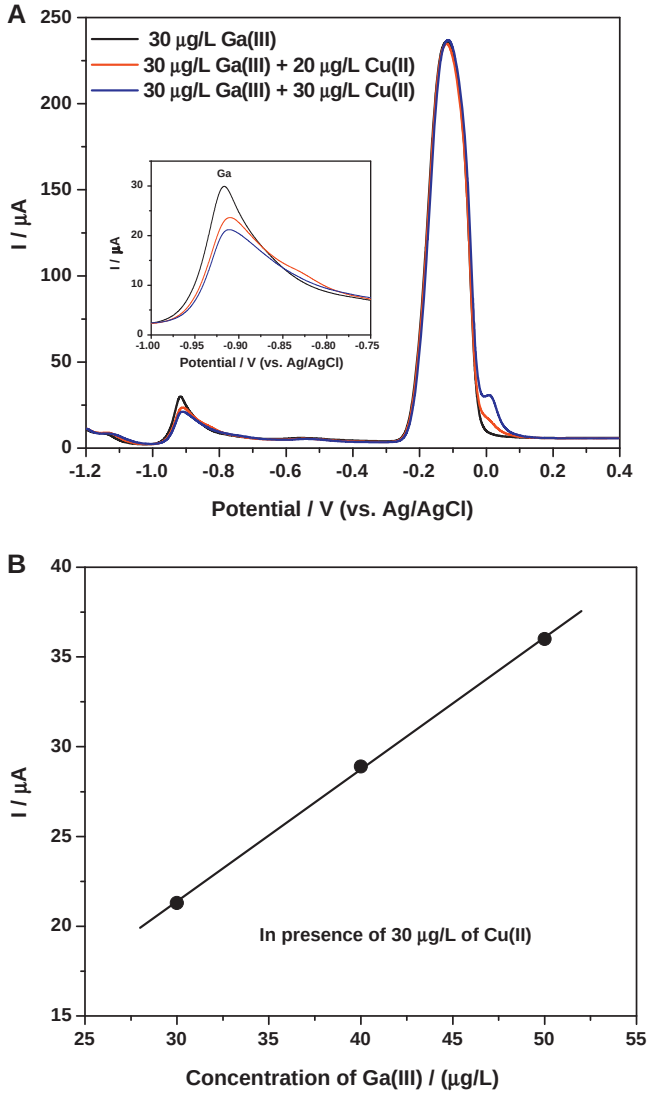

Fig. 8. (a) SWASV of 30 μg/L Ga(III) on BiFE for increasing concentration of Cu(II) (0, 20 and 30 μg/L). The other conditions are as in Fig. 2. Inset: the zoomed image of the Ga(III) stripping peak. (b) The calibration plot of gallium over the concentration range of 30–50 μg/L in presence of 30 μg/L of Cu(II).

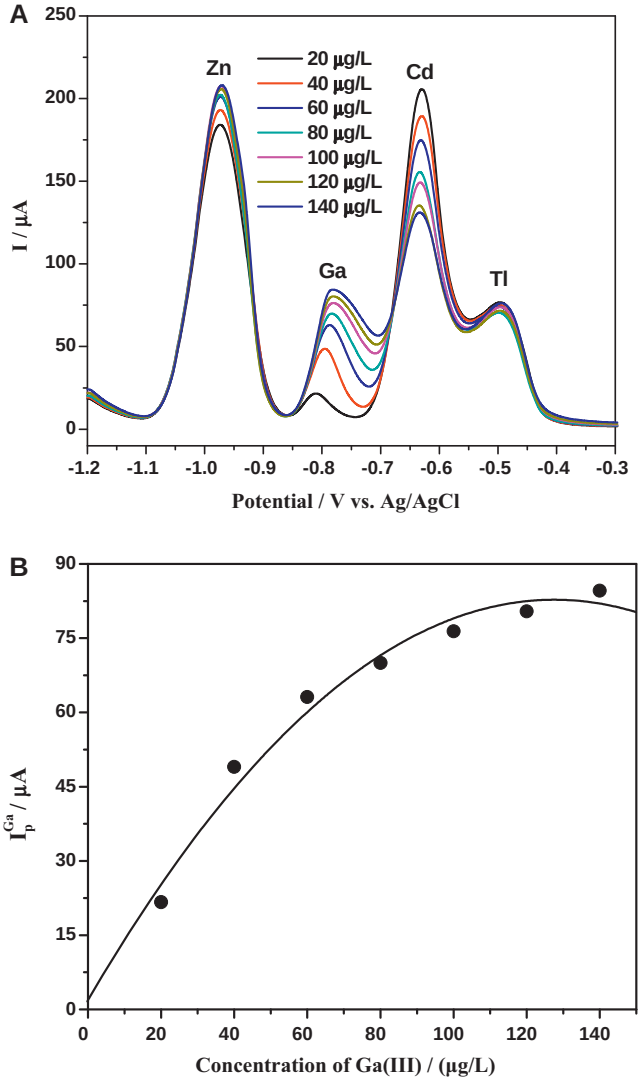

Fig. 9. (a) SWASV for increasing concentration of Ga(III) on BiFE in the concentration range between 20 and 140 μg/L in 20 μg/L steps in presence of Zn(II), Cd(II) and Tl(I) (20 μg/L each). (b) Calibration plot of gallium over the concentration range of 20–140 μg/L. The other conditions are as in Fig. 2.

obtained by least-squares regression was expressed by Eq. (4).

$$I_p(\mu A) = 1.91 + 1.268\ C(\mu g/L) + 0.005\, C^2(\mu g/L)^2 \quad (R^2 = 0.979) \tag{4}$$

A detection limit of 2.3 μg/L of Ga(III) was estimated from ten replicate determinations of blank solution under optimum conditions ($S/N = 3$). The impurities like Zn(II), Cd(II) and Tl(I) did not cause any hindrance for the determination of gallium and it offers an opportunity for the determination of gallium in presence of these impurity elements. However, concentration of gallium showed significant influence on cadmium and zinc, but thallium showed no dependency on gallium concentration. The average stripping peak current of 20 μg/L thallium in 0.2 M acetate buffer solution (pH 4.6) was observed as 74.2 μA (±2.9% RSD) in presence of 20–140 μg/L of gallium. The stripping peak current of 20 μg/L zinc in 0.2 M acetate buffer solution (pH 4.6) increased slightly from 184 μA to 209 μA for increasing gallium concentration, whereas the stripping peak current of 20 μg/L cadmium in 0.2 M acetate buffer solution (pH 4.6) decreased remarkably from 206 μA to 131 μA for the same. Fig. 10i shows the SWASV of 20 μg/L gallium on BiFE in 0.2 M acetate buffer solution (pH 4.6) in presence of 20 μg/L cadmium. Upon addition of 40 μg/L of zinc simultaneously with increasing the gallium concentration to 40 μg/L, the cadmium stripping peak was remarkably suppressed (Fig. 10ii). However, the heights of both cadmium and zinc stripping peaks were enhanced on further addition of 20 μg/L cadmium into it (Fig. 10iii).

The above observations can be attributed to the formation of solid solution of zinc with bismuth, gallium and cadmium up to 6 wt.%, 1 wt.% and 1 wt.%, respectively [38]. Since the deposition of solid solution is energetically more favourable process compared to the deposition of individual metal, thus due to the formation of Ga–Zn solid solution, the stripping peak height of zinc increased on increasing gallium concentration. When the concentration of gallium in solution was further increased, Ga–Zn solid solution formed at the expense of Zn–Cd solid solution because of the limited amount of zinc in solution. In this case, gallium is preferentially bound with zinc releasing cadmium into the bismuth matrix and this leads to the suppression of the stripping peak height of cadmium upon increasing the concentration of gallium.

A closer inspection of Fig. 10i reveals that as the gallium concentration increased in the solution, a small overlapping occurred

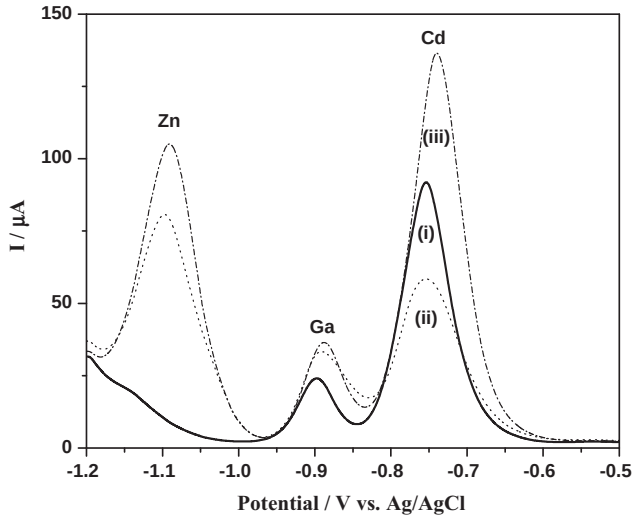

Fig. 10. SWASV of (i) 20 μg/L Ga(III) on BiFE in presence of 20 μg/L of Cd(II), (ii) 40 μg/L Ga(III) on BiFE in presence of 20 μg/L of Cd(II) and 40 μg/L of Zn(II), (iii) 40 μg/L Ga(III) on BiFE in presence of Cd(II) and Zn(II) (40 μg/L each). The other conditions are as in Fig. 2.

between the stripping peaks of gallium and cadmium. Thus the experimental data was fitted with Gaussian peaks in order to check for any improvement in the calibration data of gallium. This exercise allowed us to compare the experimental peak heights to the computed peak heights as well as to obtain the peak areas for the individual constituents of the experimental curve. The least-squares fitting with Gaussian peak produced an excellent fit and resulted in plots similar to the experimental curve. Fig. 11 shows the Gaussian fitted curve superimposed on the experimental square wave anodic stripping voltammogram for 40 μg/L Ga(III) in presence of Zn(II), Cd(II) and Tl(I) (20 μg/L each). The fitted Gaussian peak of each constituent is also shown in the same figure.

The experimental and computed peak heights are shown in Fig. S3A for gallium. The computed peak heights were observed to match closely with the experimental peak heights. The calibration curve produced by the computed data and experimental data also showed the regression coefficients (R^2) of 0.9889 and 0.9837, respectively. Thus, it can be stated that the measurement of peak

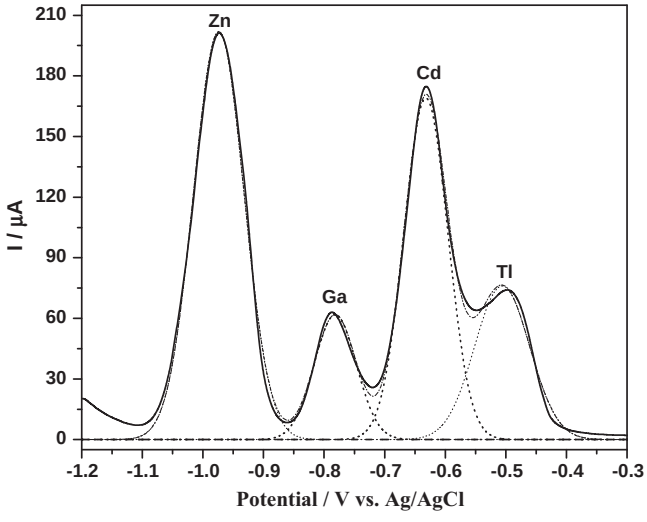

Fig. 11. Representative computed data (- - -) by using least-square Gaussian fitting algorithm superimposed on the experimental data (solid line) for SWASV of 40 μg/L Ga(III) on BiFE in presence of Zn(II), Cd(II) and Tl(I) (20 μg/L each). The peak area of each constituent is shown by dotted line (. . . .).

height of gallium from the experimental curve would be a valid analytical approach. The calibration data obtained from the peak area (A_p) of gallium revealed slightly better regression coefficient of 0.999 (Fig. S3B) compared to that from the experimentally determined peak heights. The calibration equation was expressed as Eq. (5):

$$A_p(\mu AV) = -1.15 + 0.116\,C(\mu g/L) + 0.0003\,C^2(\mu g/L)^2 \quad (R^2 = 0.999) \tag{5}$$

However, this minor improvement requires significant post experimental analysis compared to the simplicity of peak height determinations directly from the experimental curve.

4. Conclusion

The present study demonstrates the possibility of detection and determination of Ga(III) in ground water by square wave anodic stripping voltammetry on bismuth film electrode. SWASV at BiFE with the optimized experimental parameters exhibited good linear dependency in the concentration range of 20–100 μg/L and LOD of 6.6 μg/L for Ga(III). The performance of BiFE was found to be better than conventional MFE. Cu(II) was observed to interfere with the accuracy and sensitivity of Ga(III) determination. However, the determination of gallium by SWASV on BiFE in acetate buffer solution (pH 4.6) showed second order polynomial dependency in the concentration range of 20–140 μg/L and LOD 2.3 μg/L ($S/N = 3$) for Ga(III) in presence of 20 μg/L each of the potential interfering ions viz. Zn(II), Cd(II) and Tl(I). In this case, the shape of the stripping peak of cadmium showed significant deformation upon increasing gallium concentration because of the competition between the bimetallic alloy formation of zinc with cadmium and gallium. The least-squares fitting of the experimental signal with Gaussian peak produced an excellent fit. The fitting process revealed almost similar stripping peak heights as obtained from the experimentally observed data though some improvement in the calibration curve was obtained from the peak area analysis. The overall results suggest that Ga(III) can be detected as well as determined in the ground water sample by utilizing the present methodology.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.09.010.

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