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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.

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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 instrumental cost, long exposure times or matrix interferences	[13,14]
7.	X-ray fluorescence spectrometry	Several ppm	–		[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

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