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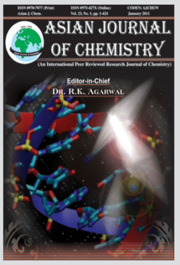

Simultaneous Determination of Indium and Aluminum by Adsorptive Stripping Voltammetry in Presence of Eriochrome Blue Black R

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A sensitive and selective method for the simultaneous determination of trace amounts of indium and aluminum by adsorptive stripping voltammetry was developed using Eriochrome blue black R [1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulfonic acid sodium salt, EBBR] as selective complexing agent on the multi-walled carbon nanotubes (MWCNTs) modified electrode. In a single scan, both metals gave peaks that were distinctly separated by 0.67 V allowing their determination in the presence of each other. Optimal analytical conditions were found to be: Eriochrome blue black R concentration of 40 μM, pH of 6.0 and adsorptive potential of -1.0 V *versus* saturated calomel electrode (SCE). With an accumulation time of 30 s, the peak currents are proportional to the concentration of indium in the range of 5.0×10^{-9} to 1.0×10^{-6} M and to that of aluminum in the range of 1.0×10^{-8} to 8.0×10^{-7} M. The detection limits (S/N = 3) are 1.0×10^{-9} and 8.0×10^{-9} M, respectively. This procedure was applied to simultaneous determination of indium and aluminum in some real samples with satisfactory results.

Key Words: Indium, Aluminum, Adsorptive stripping voltammetry, Eriochrome blue black R, Simultaneous determination.

INTRODUCTION

Aluminum is of great concern due to its large natural abundance and its possible toxic effects[1]. Aluminum is the third most abundant element at the earth crust. It is commonly found in living organism consumed as food by human beings. The naturally occurring forms are usually stable and do not interfere with biological processes. Although, excessive use of aluminum products influences the human organism negatively, it causes disturbances in calcium and phosphate metabolism and also brings damage to the bone system[2-5]. Indium is of interest for their widespread medical and radio diagnostic applications[6,7]. Indium is used as a semiconductor and because of its high plasticity, low melting point and relative stability, it is extensively used in non-ferrous metallurgical industries[8,9]. Increasing interest and importance of these metals in different fields have made it necessary to develop simple and selective methods for their determination.

Among various methods for metal ions determination, adsorptive stripping analysis offers many advantages over other analytical techniques including high sensitivity, favourable portability, suitability for automation, high speed of analysis, low power requirement and inexpensive equipment[10-14]. Many analytical procedures have been proposed for the individual determination of indium[15-19] and aluminum[20-27] on the bases including anodic stripping voltammetry and adsorptive stripping voltammetry. In spite of this fact, there are two reports on simultaneous determination of indium and aluminum by UV-visible spectrophotometer[28] and fluorescence sensor[29]. To the best of our knowledge, the simultaneous analysis of indium and aluminum by a single scan has not been reported yet. This is because the reduction potential of aluminum is more negative than that of indium, so it is easy for indium to accumulate and reduce while it is very difficult for aluminum to reduce directly in water solution. Thus, accurate determination of these two species in the presence of each other is not possible by common electroanalytical methods. Eriochrome blue black R [1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulfonic acid sodium salt, EBBR] is a dye which commonly used as a complexometric indicator for measuring the calcium and magnesium ions in water. Furthermore, it has been used for determination of benproperine phosphate[30] and protein[31] and it has also been used to chelate many metal ions for chemical analysis[32-34]. In this work, an adsorptive stripping voltammetry was introduced for simultaneous determination of indium and aluminum by using an eriochrome blue black R (Fig. 1) as a complexing agent. Various factors which influenced the simultaneous determination of aluminum and indium were investigated in detail.

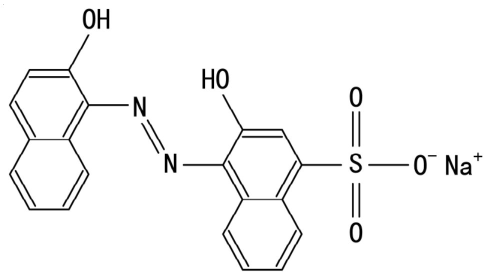

Fig. 1. Structure of eriochrome blue black R

EXPERIMENTAL

The multi-walled carbon nanotubes (MWCNTs, purity > 95 %) sample used in this work was purchased from Chengdu Organic Chemical Corporation (China). Eriochrome blue black R ($C_{20}H_{13}N_2O_5SNa$, m.w. 416.39) was purchased from Fluka Chemical Corporation and its stock solution was prepared daily. The In(III) and Al(III) stock solutions of 0.01 M were prepared by dissolving the required amounts of $In_2(SO_4)_3$ and $Al_2(SO_4)_3$ (Shanghai Reagent Corporation, China) into redistilled water and then diluted to various concentration working solutions. An acetate buffer (pH 6.0) solution of 0.01 M was always employed as a supporting electrolyte. Solutions were deaerated by bubbling high-purity nitrogen prior to the experiments. Unless otherwise stated, all chemicals and reagents used were of analytical reagent grade and all of the chemicals and reagents were used without further purification. All solutions were prepared using redistilled water.

All electrochemical measurements were carried out in a conventional three-electrode cell with a CHI650A electrochemical workstation (Shanghai Chenhua Instruments, China). Modified and unmodified glassy carbon electrodes (GCE) were used as working electrodes. A platinum electrode was used as a counter electrode and a saturated calomel electrode (SCE) served as a reference electrode.

Fabrication of the modified electrode: Pristine MWCNTs was treated by mixed acid in order to purify MWCNTs and segment MWCNTs for easier and better dispersion[35,36]. 500 mg of the pristine MWCNTs was dispersed in 100 mL of concentrated solution HNO_3/H_2SO_4 (1/3 by volume) and ultrasonicated for 2 h at room temperature. The resulting suspension was filtered with a polytetrafluoroethylene membrane disc filter (1 µm pore size) in a vacuum, followed by washing several times with redistilled water to neutralization. The MWCNTs on a membrane disc was dried in an oven at 80 ºC for 12 h. Then, ultrasonic agitation was used to disperse 10 mg treated MWCNTs into 10 mL N,N-dimethylformamide (DMF) to give a 1 mg mL^{-1} black suspension. Before each electrochemical experiment, GCE surfaces were polished using a polishing cloth and 0.05 µm alumina slurry and rinsed with doubly distilled water, HNO_3 (1/1 by volume) and anhydrous alcohol. Afterwards, the GCE was coated with 10 µL of 1 mg mL^{-1} MWCNTs-DMF suspension and the solvent evaporated under an infrared lamp for 10 min. The MWCNTs/GCE was cleaned with distilled water before use.

Procedure: All electrochemical measurements were carried out in 0.01 M acetate buffer (pH 6.0) solution containing the required amounts of metal ions and eriochrome blue black R (EBBR). A preconcentration potential of -1.0 V (*vs.* SCE) was applied to the working electrode under stirring conditions. The stirring was stopped and after 10 s equilibration time, the voltammograms were recorded between -1.2 and 1.0 V. The electrode was cleaned for 30 s at 1.0 V to remove the residual metals under stirring conditions and then the next measurement was performed. All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Adsorptive characteristics of the In-EBBR and Al-EBBR complexes: Preliminary experiments were carried out to identify the general features, which characterized the behaviours of the metal ions and EBBR on the MWCNTs/GCE. Fig. 2 shows the cyclic voltammograms of 0.8 µM indium and 0.6 µM aluminum (curve a) and their complexes with 40 µM EBBR (curve b) at pH 6.0 after 30 s accumulation at -1.0 V. The forward potential scan commences at an initial potential of -1.2 V and its direction was reversed at 1.0 V. In the absence of EBBR conditions (curve a), the redox peaks of indium appear on cyclic voltammograms, while there are no redox peaks of aluminum on cyclic voltammograms. When EBBR was added in (curve b), redox peaks currents of indium increased less and redox peaks potentials shifted slightly, while redox peaks of aluminum appeared synchronously. The shift in the peaks potentials of indium complex and the appearance of the redox peaks of aluminum complex are due to formation of coordinated compounds between metal ions and ligand. In addition, the reduction potential of Al-EBBR complex is more positive than that of aluminum ions and it is beneficial to the reduction of aluminum with EBBR. As the current of Al-EBBR increased larger than that of In-EBBR, it indicated aluminum had greater complexing capacity with EBBR. Nevertheless, the closeness of the oxidation to the reduction peak potentials showed that the redox processes for indium (peak separation of 0.03 V) is reversible.

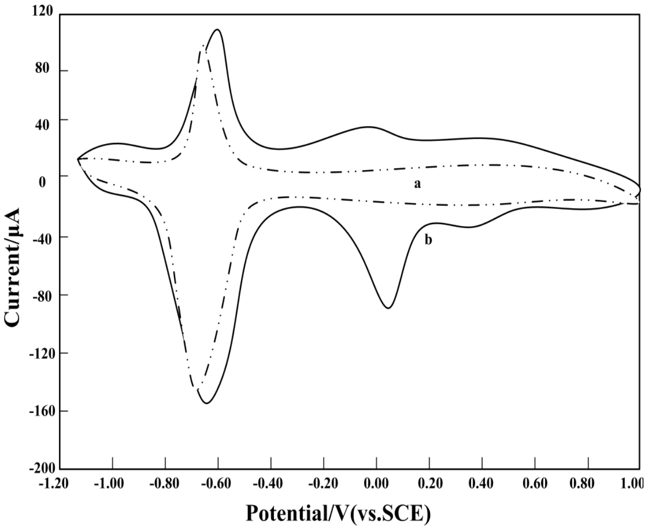

Fig. 2. Cyclic voltammograms of 0.01 M acetate buffer (pH 6.0) containing (a) 0.8 µM In(III) and 0.6 µM Al(III); (b) (a) + 40 µM eriochrome blue black R, with scan rate of 100 mV s^{-1}

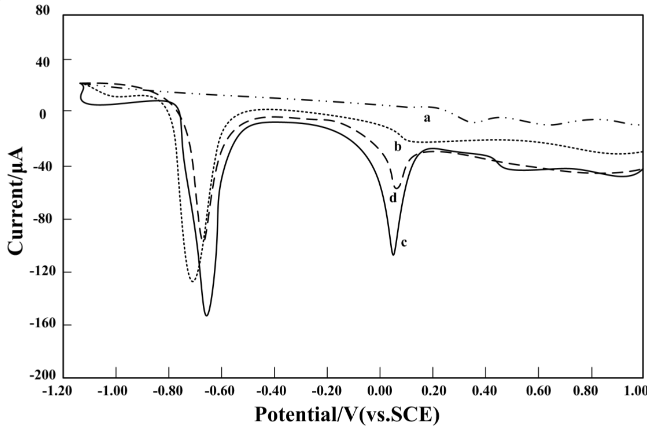

Fig. 3. Adsorptive stripping voltammograms of: (a) 40 μM of eriochrome blue black R solution at pH 6.0 after 30 s accumulation time at -1.0 V; (b) 0.8 μM In(III) and 0.6 μM Al(III) under similar experimental conditions as (a); (c) (a) + (b) under similar experimental conditions as (a); and (d) solution (c) without accumulation time, with scan rate of 100 mV s^{-1}

Fig. 3a displays adsorptive stripping voltammogram of 40 μM EBBR solution at pH 6.0 (acetate buffer) after 30 s accumulation at -1.0 V. In Fig. 3b the voltammogram of a solution containing 0.8 μM In(III) and 0.6 μM Al(III) under similar experimental conditions is shown. The voltammograms of the mixture of 40 μM EBBR, 0.8 μM In(III) and 0.6 μM Al(III) with 30 s accumulation time (Fig. 3c) and without accumulation time (Fig. 3d) are also shown. As illustrated in Fig. 3, the sensitivity of indium and aluminum stripping currents enhanced due to the addition of EBBR to the solution. These responses increased when an accumulation time preceded the potential scan. These stripping currents increased linearly with increasing metal concentrations. With respect to the facts that the metal stripping currents increased due to the addition of EBBR to the solution and the dependence of peak current on the accumulation time, it can be concluded that the metal-EBBR complexes were adsorbed on the surface of electrode. In conclusion, both metals gave peaks that were distinctly separated by 0.67 V allowing their determination in the presence of each other by a single scan.

Choice of supporting electrolyte: In this work, the adsorptive stripping responses of In(III)-EBBR and Al(III)-EBBR in a variety of supporting electrolytes, such as KCl, KNO_3, Na_2SO_4, NH_4Cl, HCl, H_2SO_4, AcOH, NaOAc and acetate buffer solution, phosphate buffer solution (each 0.01 M), were compared. It was found that the stripping peak current was highest in 0.01 M acetate buffer solution and synchronously the stripping peak shape was best defined. Therefore, a 0.01 M acetate butter solution was selected as the supporting electrolyte for the simultaneous determination of indium and aluminum. Fig. 4 shows the effect of solution pH on adsorptive stripping peak currents of In(III)-EBBR and Al(III)-EBBR in the pH range from 3.0 to 9.0. The stripping peak currents of both In(III)-EBBR and Al(III)-EBBR increase with increasing solution pH first and then decrease with increasing solution pH further. The increases in stripping peak currents with increasing solution pH are ascribed to the preconcentration of In(III)-EBBR and Al(III)-EBBR, which is promoted on electrode surface. The decreases in the stripping peak currents of both In(III)-EBBR and Al(III)-EBBR at high pH are most probably due to hydrolysis of In(III)-EBBR and Al(III)-EBBR in acetate medium. So, pH 6.0 was selected for subsequent experiments.

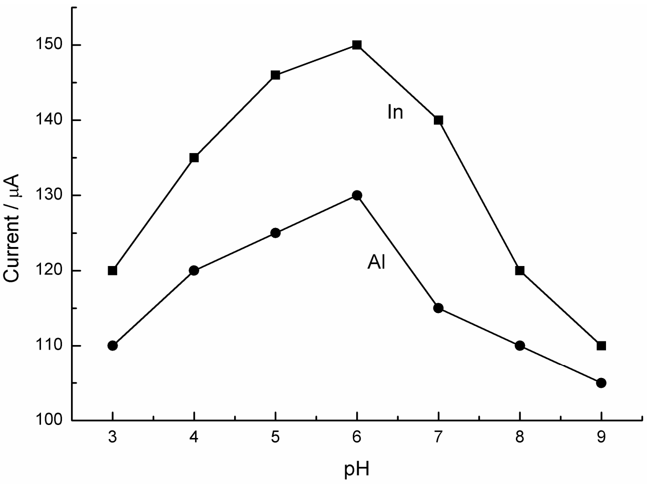

Fig. 4. Effect of pH on the stripping peak currents of 0.8 μM In(III) and Al(III) in the presence of 40 μM EBBR and after 30 s accumulation time at -1.0 V

Effect of EBBR concentration: The dependence of the In(III)-EBBR and Al(III)-EBBR peaks currents on the complexing agent concentration was tested. The EBBR ranged from 5 to 100 μM in the presence of 0.8 μM In(III) and Al(III) and 0.01M acetate buffer as supporting electrolyte (pH 6.0). Fig. 5 shows that the peaks currents of In(III)-EBBR and Al(III)-EBBR complexes increase along with increasing of the EBBR concentration up to 40 μM. At concentrations higher than 40 μM both the peaks keep constant as a consequence of a full electrode surface coverage. Consequently, an optimum EBBR concentration of 40 μM was selected for further experiments.

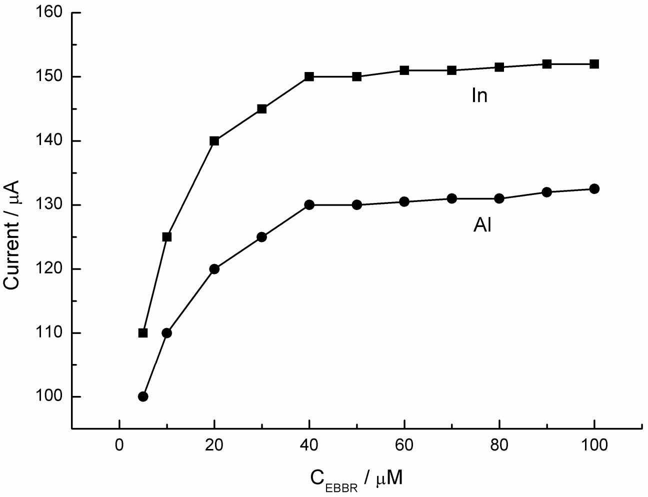

Fig. 5. Effect of EBBR concentration on the stripping peak currents of 0.8 μM In(III) and Al(III) at pH 6.0. Other conditions as in Fig. 4

Effect of accumulation parameters: The effect of accumulation potential on the stripping peak currents of aluminum and indium complexes with EBBR was examined individually over the potential range of -0.2 to -1.4 V. The plots of stripping peak currents of both metal ions as a function of preconcentration potential are shown in Fig. 6. As it is shown obviously the peak currents increased up to about -0.8 and -1.0 V for indium and aluminum respectively and decreased with going toward more negative values. The accumulation potential of -1.0 V was used in all further measurements. Variation of the deposition time between 0 and 100 s at a deposition potential of -1.0 V shows that by increasing accumulation time up to 30 s, the peak currents of both metal ions increase, whereas after 30 s the peak current of indium increases but the peak current of aluminum decreases slightly (Fig. 7). This behaviour is due to competitive adsorption behaviour between In(III)-EBBR and Al(III)-EBBR in the adsorption on the electrode surface. Thus, deposition time of 30 s was used throughout, as it combines good sensitivity and relatively short analysis time. The effect of the scan rate was also tested in the range from 10 to 300 mV s^{-1}. As the scan rate increased, the peak current increased. But at high scan rates, the background current also increased. The signal-to-noise ratio was at maximum while the scan rate was 100 mV s^{-1}, so 100 mV s^{-1} was chosen in this work.

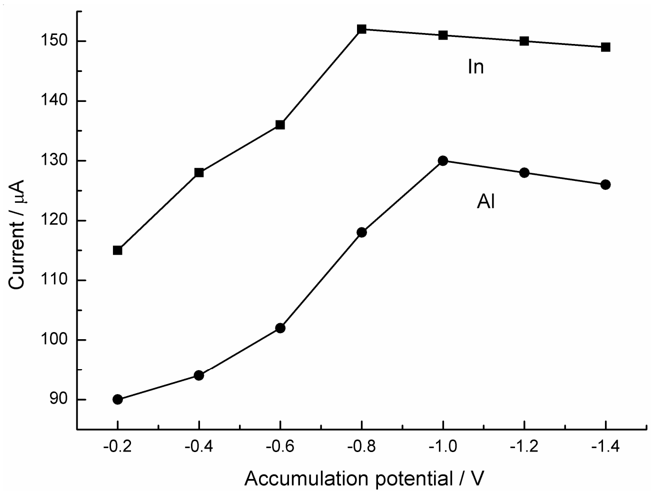

Fig. 6. Effect of accumulation potential on the stripping peak currents of 0.8 μM In(III) and Al(III) in the presence of 40 μM EBBR. Other conditions as in Fig. 5

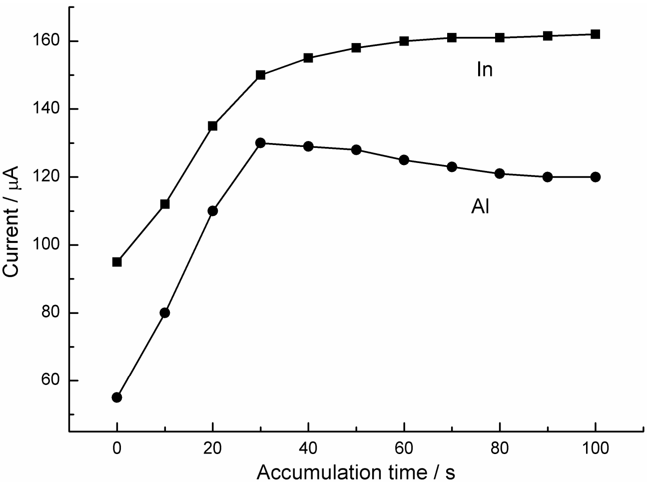

Fig. 7. Effect of accumulation time on the stripping peak currents of 0.8 μM In(III) and Al(III) at -1.0 V. Other conditions as in Fig. 6

Linear range, detection limit and repeatability: To verify the linear relationship between peak currents and metal ions concentration, four calibration graphs were constructed under optimum conditions. The calibration graphs were performed for indium and aluminum separately and in the presence of each other (Figs. 8 and 9). In addition, the simultaneous calibration graph was presented in Fig. 10. The results of this study (correlation coefficients greater than 0.99) indicated that in all cases the current-concentration relationships were linear in the concentration range of $5.0 \times 10^{-9} – 1.0 \times 10^{-6}$ M and $1.0 \times 10^{-8} – 8.0 \times 10^{-7}$ M for indium and aluminum, respectively. The 3σ-detection limits calculated using an accumulation time of 30 s were 1.0×10^{-9} M for indium and 8.0×10^{-9} M for aluminum.

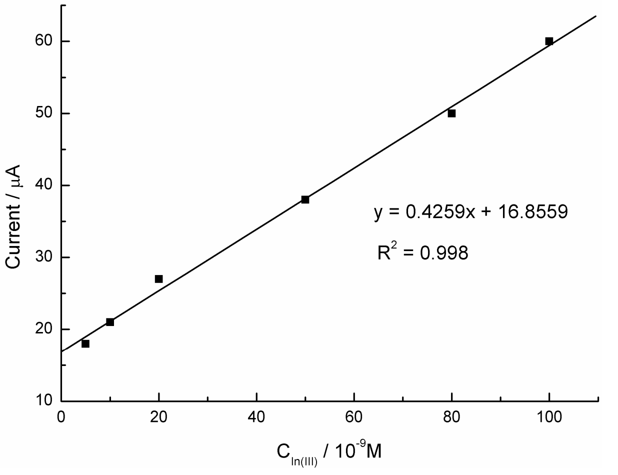

Fig. 8. Calibration plot of In(III) in the presence of 0.1 μM aluminum ion at optimum conditions (pH = 6.0, EBBR = 40 μM, accumulation potential = -1.0 V, accumulation time = 30 s and scan rate = 100 mV s^{-1})

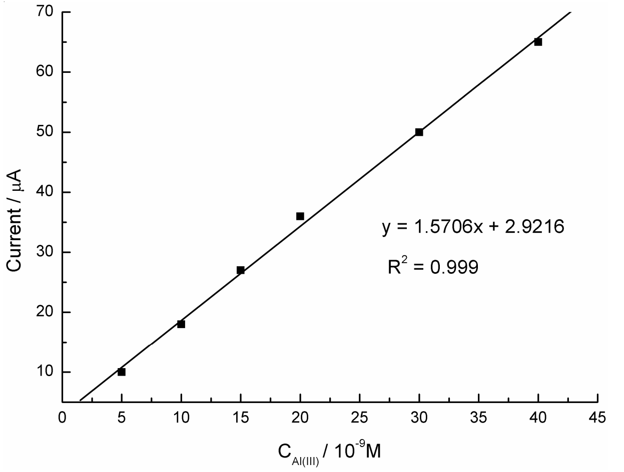

Fig. 9. Calibration plot of Al(III) in the presence of 0.1 μM indium ion at optimum conditions (pH = 6.0, EBBR = 40 μM, accumulation potential = -1.0 V, accumulation time = 30 s and scan rate = 100 mV s^{-1})

The repeatability of the method was estimated by ten successive measurements of two solutions containing 0.8 μM In(III) and Al(III) under the optimized conditions. The relative standard deviations of 3.5 and 2.4 % were obtained for In(III) and 3.8% and 1.9% for Al(III), respectively.

TABLE-2
DETERMINATION OF INDIUM AND ALUMINUM IN WATER SAMPLES

Sample	Added (10^{-9} M)		Found (10^{-9} M)[a]		Recovery (%)		Found (10^{-9} M)[b]	
	In(III)	Al(III)	In(III)	Al(III)	In(III)	Al(III)	In(III)	Al(III)
River water	-	-	8.52 ± (0.25)	35.03 ± (0.12)	–	–	8.55 ± (0.10)	35.05 ± (0.08)
	10.0	20.0	18.38 ± (0.22)	54.92 ± (0.17)	99.2	99.8		
	20.0	40.0	28.21 ± (0.20)	75.18 ± (0.12)	98.9	100.2		
Tap water	-	-	< LOD[c]	45.56 ± (0.08)	–	–	< LOD	45.58 ± (0.10)
	10.0	20.0	10.18 ± (0.18)	64.32 ± (0.10)	101.8	98.1		
	20.0	40.0	20.25 ± (0.16)	84.86 ± (0.10)	101.3	99.2		
Well water	-	-	10.60 ± (0.25)	68.32 ± (0.15)	–	–	10.62 ± (0.09)	68.36 ± (0.08)
	10.0	20.0	20.23 ± (0.22)	85.25 ± (0.13)	98.2	96.5		
	20.0	40.0	30.48 ± (0.20)	106.30 ± (0.16)	99.6	98.1		

[a]Numbers in the parenthesis show the standard deviation for a five replicate measurements; [b]The results of ICP measurements; [c]Limit of detection.

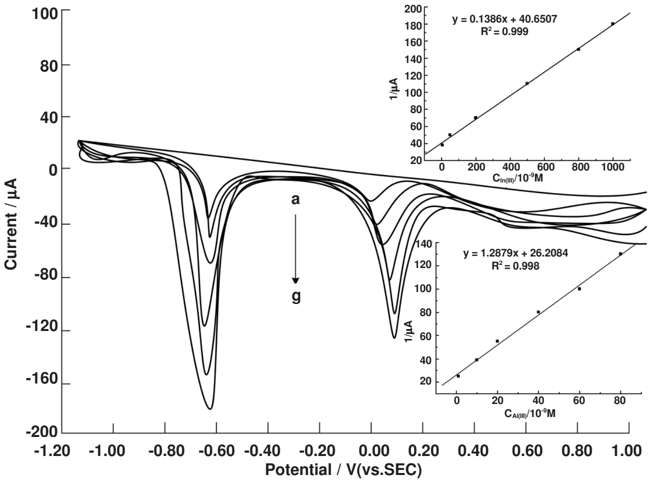

Fig. 10. Adsorptive stripping voltammograms of different concentrations of In(III) and Al(III): (a) 0, 0 µM, (b) 0.005, 0.010 µM, (c) 0.050, 0.100 µM, (d) 0.200, 0.200 µM, (e) 0.500, 0.400 µM, (f) 0.800, 0.600 µM and (g) 1.000, 0.800 µM, respectively, at optimal conditions (pH = 6.0, EBBR = 40 µM, accumulation potential = -1.0 V, accumulation time = 30 s and scan rate = 100 mV s^{-1})

Interferences studies: Possible interference by other inorganic ions with the adsorptive stripping voltammetry of indium and aluminum was investigated by the addition of the interfering ion to a solution containing these metals at the optimum conditions. The results of this study are summarized in Table-1. As it is seen that all cations and anions were tested as interferents did not significantly influence the determination of 0.8 µM of each metal ion. Interference due to surfactants such as sodium dodecyl sulfate (SDS) and Triton X-100 was tested. The results showed that 50-fold (by weight) of SDS did not significantly influence the height of the peak currents. The peak heights decreased to more than 40 % of the initial value when 10-fold of Triton X-100 was added to the sample solution and were completely suppressed with addition of 20-fold of Triton X-100.

Real sample analysis: To evaluate the validity of the proposed method for real sample analysis, the proposed procedure was successfully applied to the simultaneous determination of indium and aluminum in water samples (river water, tap water, well water). The standard addition method was used for testing recovery. Tables-2 shows that analytical values obtained by this method are in good agreement with the data obtained by ICP-AES. The results also suggest that the recoveries of this method are satisfactory and simultaneous determination of indium and aluminum using this method is feasible.

TABLE-1
TOLERANCE LIMIT TO FOREIGN IONS ON THE DETERMINATION OF 0.8 µM OF INDIUM AND ALUMINUM ION UNDER OPTIMUM CONDITIONS

Foreign ions	Tolerance limit (µM)	
	Indium	Aluminum
K^+, Na^+, Mg^{2+}, I^-, Cl^-, Br^-, ClO_3^-, ClO_4^-, NO_3^-	800	10
Ca^{2+}, Cd^{2+}, Sn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}	500	200
Pd^{2+}	200	50
Mn^{2+}	100	20
Cu^{2+}	100	800
Zn^{2+}	20	500
Bi^{3+}	50	200
F^-, CN^-	30	100

Conclusion

The present study demonstrates that adsorptive stripping voltammetry of aluminum and indium based on accumulation of In-EBBR and Al-EBBR complexes on MWCNTs/GCE can be used for determining trace amounts of both elements in the presence of each other. The method offers a practical potential for simultaneous determination of trace amounts of aluminum and indium in a single scan with high selectivity and sensitivity, simplicity and speed that have not been presented together in the previously reported systems.

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