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Journal:	*Analytical Methods*
Manuscript ID	AY-ART-03-2016-000621
Article Type:	Paper
Date Submitted by the Author:	02-Mar-2016
Complete List of Authors:	Wasąg, Joanna; Uniwersytet Marii Curie-Sklodowskiej, Faculty of Chemistry Grabarczyk, Malgorzata; maria Curie-Sklodowska University,

Journal Name

ARTICLE

Adsorptive stripping voltammetry of In(III) in the presence of cupferron using in situ plated bismuth film electrode

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

A sensitive and selective method for the determination of trace concentration of indium in natural water samples using adsorptive stripping voltammetry at an in situ plated bismuth film electrode was described. The procedure applied cupferron as a complexing agent and was based on simultaneous bismuth film formation and In(III)-cupferron complex preconcentration at -0.65 V and its cathodic stripping during the potential scan. Experimental conditions such as the concentration of cupferron, the pH of the supporting electrolyte, conditions of bismuth film formation, accumulation potential and accumulation time were established. The optimum analytical conditions included: 0.1 mol L^{-1} acetate buffer (pH = 4.5), 1×10^{-4} mol L^{-1} cupferron, 4×10^{-4} mol L^{-1} bismuth. The calibration graph was linear from 5×10^{-9} mol L^{-1} to 5×10^{-7} mol L^{-1} for accumulation time of 60 s. The detection limit was 1.6×10^{-9} mol L^{-1} with the correlation coefficient of 0.998. The influence of interfering substances such as surfactants and humic substances present in the matrices of natural water samples was studied. The proposed method was validated in the course of In(III) recovery determination from spiked natural water samples like river water and lake water.

1. Introduction

Indium in metallic form is a silvery-white solid which was considered for a long time to be a rare, nonessential and useless element. In the past it was used as an additive to steel alloys, for the production of resistance thermometers, optical instruments and as a component of metallic anticorrosion coating. However, in each of those applications it can be replaced by another readily available metal.[1,2] In recent years indium has gained importance in the field of electronics in high-technology industries. Some indium alloys have superconducting properties and are used in the production of semiconductors, infrared detectors, high-efficiency photovoltaic devices and high-speed transistors. Indium-tin-oxide was applied in the production of touch panels with liquid crystal display screens (LCDs) that are used in computers, games, flat panel displays, CD/DVD devices, or cell phones. All those devices have the display surface covered with a thin film of indium. Also, thin coating indium oxide is used in solar cells, electroluminescent lamps, plasma displays, cathode-ray tubes, energy efficient windows, gas sensors and on aircraft and automobile windshields for deicing and demisting. In the first decade of the twenty-first century there was a rapid increase in the production of indium due to its use in the electronic industry and in the production of LCD displays.[3-5] There is little information about health effects to humans or animals that arise from exposure to indium compounds. Indium tin oxide may cause lung damage as well as irritation and burns to the skin or eyes. Oral ingestion can cause serious burns to the gastrointestinal track whereas inhaling may cause respiratory problems. According to the reports, most of the harmful effects on human body result from occupational exposure of people who work in processing plants where indium tin oxide is used. Indium may accumulate in the liver or spleen via blood and lead to chronic health effects. In animal studies (on rats and rabbits) when indium oxide was injected intravenously the researchers observed necrotizing pneumonia, early fibrosis, hyperplasia in the lung, dystrophic changes in the liver and changes in the heart.[5] It is expected that in the future the demand for indium will continue to increase and hence the potential occupational exposure to indium compounds has attracted considerable attention.[6] As concerns the environmental problems, indium can cause soil and water contamination and be very harmful to living things. Therefore, it is necessary to obtain information about the concentration of this element in different environmental samples and develop procedures that will determine trace amounts of indium.

Electrochemical stripping procedures such as anodic stripping voltammetry (ASV)[7-16] and adsorptive stripping voltammetry (AdSV)[17-20] were described for the determination of indium. Stripping voltammetry is a powerful technique for the determination of trace metals in environmental samples. The major advantages of these methods are simple and cheap

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apparatus featuring fast response and high sensitivity. Up to now in trace determination of indium the anodic stripping voltammetry (ASV) was mostly used. For this purpose the following electrodes were employed as the working electrode: hanging mercury drop electrode (HMDE),[7-11] mercury film electrode (MFE),[7] mercury-bismuth film electrode (HgBiFE),[12] bismuth film electrode (BiFE),[13] and antimony film electrode (SbFE).[14-16] In recent years several adsorptive stripping voltammetry (AdSV) procedures have been developed including those for trace determination of indium. This method allows one to obtain the low detection limit voltammetry with adsorptive preconcentration of the complex of the determined metal and it is much preferred to the accumulation of the metal on the electrode surface. In the literature several complexing agents for adsorptive accumulation of indium were employed such as morin,[17] xylenol orange,[18] APDC[19] **and cupferron.**[**20**] In all those papers about AdSV procedures[17-20] the adsorption of indium on **mercury** electrode was used.

This article describes for the first time a very sensitive and selective method for the determination of In(III) by AdSV using cupferron as a complexing agent and the in situ plated bismuth film electrode as a working electrode. Cupferron is widely used in AdSV procedures as a complexing agent because it forms stable complexes with many metals and allows one to develop a sensitive method of trace determination of this element.[21-23] It was also used to produce electroactive complexes with indium and was also employed in the adsorptive voltammetric procedure using a renewable mercury film silver based electrode (Hg(Ag)FE) which has a human-friendly construction.[20,24] The major drawback of mercury electrodes is their high toxicity. That is why, although otherwise they are almost ideal for voltammetric procedures, have good adsorptive properties and the ideally smooth surface, they must be replaced by less toxic ones.[25-27] Among the newly proposed electrodes the BiFE seems to be an attractive alternative to substitute for HMDE. It is characterized by simple in situ preparation, high sensitivity, well defined and undistorted stripping voltammetry signal, insensitivity to the presence of oxygen and above all very low toxicity. This type of film electrode was introduced to stripping voltammetry in the year 2000.[28,29] Analytical applications of the BiFE electrode were described in the literature for trace metal determination.[30-**32**] In the literature we found only a few papers that described metal determination using adsorptive stripping voltammetry, and none that would describe In(III) determination.[33-36]

An additional purpose of this study was to investigate the influence of organic substances which could disturb the voltammetric signals even at low concentrations.[37,38] In order to eliminate those interferences an additional step of mixing the sample with resin Amberlite XAD-7 was introduced in the proposed procedure. Also, the impact of foreign ions which might be present in the matrix samples was examined. Hence the proposed procedure can be applied for direct determinations in environmental water samples containing complex matrix.

2. Experimental

2.1. Apparatus

The experiments were carried out using a µAutolab PGSTAT 10 analyzer (Utrecht, The Netherlands). The classical three-electrode quartz cell consisted of a glassy carbon electrode as the working electrode, a Pt wire as an auxiliary electrode and an Ag/AgCl reference electrode (saturated NaCl). The glassy carbon electrode of 1-mm diameter was polished daily on 2000 grit sandpaper whereupon using 0.3 µm alumina slurry on the Buehler polishing pad.

2.2. Reagents

All chemicals used were of analytical grade or Suprapure and the solutions were prepared with triply distilled water. The In(III) solutions for testing and calibration were prepared every day by dilution as required of the stock standard solution of 1 g L^{-1} which was obtained from Fluka (Buchs, Switzerland). Cupferron (benzenamine, N-hydroxy-N-nitroso-ammonium salt) was purchased from Merck (Darmstadt, Germany). A solution of 1×10^{-2} mol L^{-1} of cupferron was prepared every day by dissolving 0.031 g of the reagent in water in a 20 mL volumetric flask. The acetate buffer was prepared from Suprapure NaOH whereas CH_3COOH was obtained from Merck. A standard solution of 1 g L^{-1} Bi(III), Triton X-100, sodium dodecyl sulphate (SDS), cetyltrimethylammonium bromide (CTAB) were purchased from Fluka (Buchs, Switzerland). Humic acid sodium salt (HA) was obtained from Aldrich, natural organic matter (NOM) and river fulvic acid (FA) were obtained from the Suwannee River and purchased from the International Humic Substances Society. Biosurfactant (Rhamnolipids) and Amberlite XAD-7 resin was obtained from Sigma (St. Luis, MO, USA). Amberlite XAD-7 was washed four times with triply distilled water before use and dried at the temperature of 50 °C.

2.3. Voltammetric procedure

Standard experiments were performed using differential pulse adsorptive stripping voltammetry (DP-AdSV) in the following manner. A sample solution containing 1 mL of 1 mol L^{-1} acetate buffer (pH = 4.5), 800 µL of 1 g L^{-1} Bi(III) and 100 µL of 1×10^{-2} mol L^{-1} cupferron was transferred to the voltammetric cell and the solution was diluted to 10 mL with triply distilled water. The final concentrations of reagents were equal to 0.1 mol L^{-1} acetate buffer, 4×10^{-4} mol L^{-1} Bi(III) and 1×10^{-4} mol L^{-1} cupferron. The measurements were carried out from undeaerated solutions. The accumulation of In(III) was carried out at -0.65 V for 60 s. During that step the bismuth film was plated on the glassy carbon electrode and the In(III)-cupferron complex was accumulated on the electrode whilst stirring the solution with a magnetic stirring bar. After the equilibration time of 5 s, the differential pulse voltammogram was recorded, while the potential was scanned from -0.5 V to -1.0 V. The intensity of the obtained peak was directly proportional to the concentration of In(III) in the sample. The measurements were performed at a scan rate of 200 mV s^{-1} and pulse height 100 mV. Before each measurement the electrochemical cleaning was carried out in the following way: -1.4 V for 15 s and +0.3 V for 15 s. During the first step the remains from the previous measurement were reduced to the metallic state and then they were stripped from the electrode. The In(III) peak appeared at ~-0.8 V.

3. Results and discussion

In the earlier literature it was documented that indium forms stable complexes with cupferron.[20] In this work preliminary experiments showed that those complexes were adsorbed on the in situ plated bismuth film electrode and produced a reduction peak at the differential pulse voltammogram. In order to achieve the best performance, an optimization study was carried out with the formation of in situ plated bismuth film and voltammetric measurements were performed of In(III), pH of the supporting electrolyte, the concentration of cupferron, deposition potential and deposition time of the indium complexes at the scan rate.

3.1. Effect of pH and concentration of supporting electrolyte

In the voltammetric procedure based on adsorptive accumulation of the cupferron complex with different metal ions an acidic medium was suggested.[39,40] The stability of the complexes and the potential of the reduction peak were found to be strongly dependent upon the pH value of the solution.[41] Thus, the influence of pH of the stripping process on the indium voltammetric signal in the proposed procedure was examined. As it was proved in previous experiments using cupferron as a complexing agent the optimum indium peak was observed in the presence of acetic acid and acetate buffer.[19] The measurements were performed for the samples containing a fixed concentration of 1×10^{-4} mol L^{-1} cupferron, 4×10^{-4} mol L^{-1} Bi(III), 1×10^{-7} mol L^{-1} In(III) and 0.1 mol L^{-1} acetic acid (pH = 2.87) or acetate buffer with a variable pH value in the range from 3.0 to 6.25. In the case of acetic acid no peak was observed. The obtained data for acetate buffers are shown in Fig. 1 and on this basis we were able to observe that the extreme, narrowest and most symmetric signal was achieved in acetate buffer at pH = 4.5. Also at that pH value the acetate buffer had the highest buffer capacity and so that supporting electrolyte was chosen for further experiments.

The influence of the concentration of acetate buffer at pH = 4.5 on the peak current of indium was examined in the range from 0.05 mol L^{-1} to 0.2 mol L^{-1}. The measurement was performed using a standard solution containing 1×10^{-4} mol L^{-1} cupferron, 4×10^{-4} mol L^{-1} Bi(III), 1×10^{-7} mol L^{-1} In(III). It was observed that the peak of indium did not appear at the concentration of acetate buffer up to 0.05 mol L^{-1}. At a higher concentration the peak current increased and remained the same at the concentration from 0.1 mol L^{-1} to 0.2 mol L^{-1}, thus the concentration of 0.1 mol L^{-1} was chosen for further experiments.

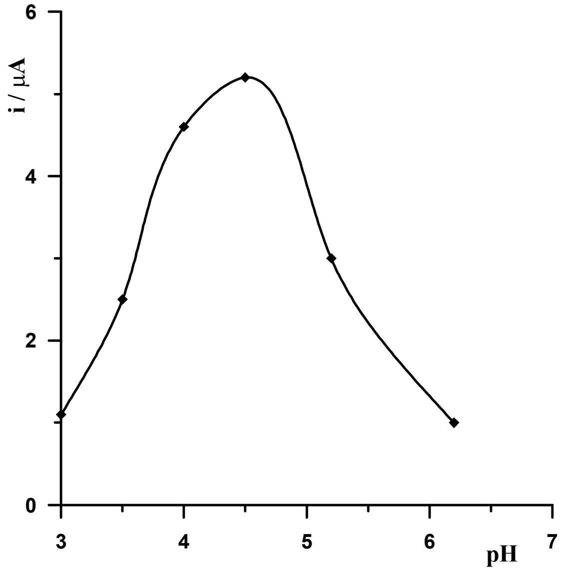

Figure 1. The influence of pH on the 1×10^{-7} mol L^{-1} In(III). Composition of solution 1×10^{-4} mol L^{-1} cupferron, 4×10^{-4} mol L^{-1} Bi(III) and 0.1 mol L^{-1} CH_3COOH/CH_3COONa. Accumulation potential -0.65 V, accumulation time 60 s.

3.2. Effect of cupferron concentration

Cupferron concentration had a considerable effect on the sensitivity of the adsorptive voltammetric method. The effect of cupferron concentration varied from 1×10^{-5} mol L^{-1} to 3×10^{-4} mol L^{-1} while the other conditions were constant: 4×10^{-4} mol L^{-1} Bi(III), 1×10^{-7} mol L^{-1} In(III), 0.1 mol L^{-1} supporting electrolyte. The results showed that the peak current increased upon increasing the cupferron concentration to 1×10^{-4} mol L^{-1} and then it slightly decreased at a higher concentration, as illustrated in Fig. 2. On the basis of these results the concentration of 1×10^{-4} mol L^{-1} was adopted as the optimum one for further measurements.

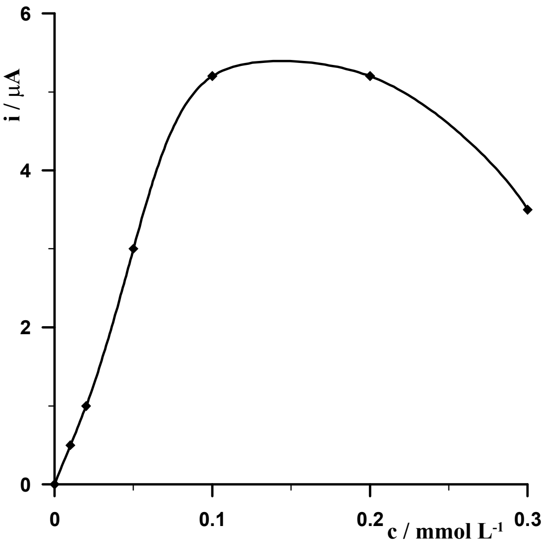

Figure 2. The influence of cupferron concentration on the In(III) signal. Concentration of In(III) 1 × 10^{-7} mol L^{-1}. Accumulation potential -0.65 V, accumulation time 60 s.

3.3. Effect of accumulation of In(III)-cupferron complex and bismuth film formation

The dependence of accumulation potential on the voltammetric peak current of the In(III)-cupferron complex and the effect of accumulation potential on bismuth film formation were examined. For this purpose standard solutions were used containing 1 × 10^{-4} mol L^{-1} cupferron, 4 × 10^{-4} mol L^{-1} Bi(III), 1 × 10^{-7} mol L^{-1} In(III) and 0.1 mol L^{-1} acetate buffer. In the previous paper concerning voltammetric procedures at the in situ plated bismuth film electrode the optimum potential for bismuth film formation ranged from -0.28 V to -0.7 V.[29,30,42]

In the first step of investigations the potential of bismuth film formation changed when the accumulation potential of indium complexes was constant and was equal to -0.65 V. The potential of bismuth film formation was then examined in the range from -1.0 V to -0.5 V with deposition time of 30 s. The obtained results show that the optimum potential for bismuth film formation was -0.65 V. In the case of lower or higher potential values for bismuth film formation the indium peak height and shape were observed to slightly decrease and deteriorate, thus the potential of -0.65 V was chosen for further measurements.

Next the accumulation potential of the In(III)-cupferron complex was examined while the potential of bismuth film formation was constant and was equal to -0.65 V. The second potential was changed from -0.9 V to -0.5 V with accumulation time of 30 s. It was observed that for the accumulation potential from -0.7 V to -0.6 V the peak of indium was the same and for lower or more negative potentials the peak height slightly decreased. So the potential of -0.65 V was chosen as the most appropriate for the standard conditions. Summing up, the same potential was applied for simultaneous in situ plated bismuth film formation and accumulation of the indium complex.

Furthermore, the effect of deposition time was examined, because this is one of the parameters that significantly affect the sensitivity in stripping voltammetry. Accumulation time was changed from 10 s to 180 s. Accumulation potential was equal to -0.65 V while the other standard conditions were the same as previously described. The value of the peak current increased linearly up to 90 s and then in the case of prolonged accumulation times the peak of indium increased insignificantly. In our experiments we performed measurements with accumulation time of 60 s, which allowed us to reduce total time of the measurements.

3.4. Effect of bismuth concentration

The Bi(III) concentration used for in situ plated bismuth film formation was found to affect the peak height for the In(III)-cupferron complex. In order to choose the optimum concentration of Bi(III) the solutions containing 1 × 10^{-7} mol L^{-1} In(III), 0.1 mol L^{-1} acetate buffer at pH = 4.5, 1 × 10^{-4} mol L^{-1} cupferron and different concentrations of bismuth were employed using deposition potential and accumulation time equal to -0.65 V and 60 s, respectively. The measurements were performed for the range of Bi(III) concentration from 1 × 10^{-4} mol L^{-1} to 5 × 10^{-4} mol L^{-1}. The measurements proved that the signal of indium was not observed on the voltammogram when Bi(III) was absent in the solution. The effect of bismuth concentration on the indium peak height is illustrated in Fig. 3. It was found that the peak of indium increased with the increase of bismuth concentration but at higher concentrations the peak shape became worse and wide. For further measurements the concentration of Bi(III) equal to 4 × 10^{-4} mol L^{-1} was applied as the optimum concentration permitting the maximum signal of indium and preferred peak shape.

3.5. Effect of scan rate

The scan rate also affects peak intensity and so it was also examined. A linear dependence was found between peak intensity and the increase of the scan rate. The scan rate was changed from 20 to 400 mV s^{-1}. At higher values the peak shape deteriorated so the scan rate of 200 mV s^{-1} was used for further measurements, to evaluate the sensitivity of the proposed procedure.

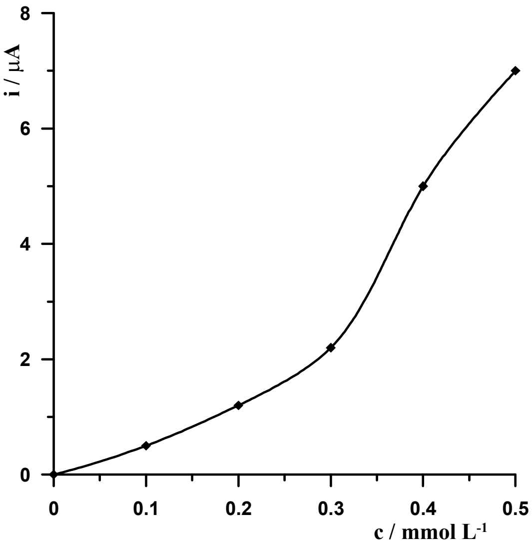

Figure 3. The influence of bismuth concentration on the In(III) signal. Concentration of In(III) 1 × 10^{-7} mol L^{-1}. Accumulation potential -0.65 V, accumulation time 60 s.

3.6. Analytical characterization

Analytical characterization of the proposed procedure was performed as concerns calibration graph, detection limit, precision (repeatability and reproducibility), ruggedness and robustness.

Calibration graph

The calibration graph for In(III) determination was determined in triply distilled water under the optimum conditions for two accumulation times of 60 s and 90 s. The linear range for the accumulation time of 60 s was linear in the range from 5 × 10^{-9} mol L^{-1} to 5 × 10^{-7} mol L^{-1} and obeyed the equation y = 53.07x + 0.23, where y is the peak current (μA) and x is the In(III) concentration (μmol L^{-1}). The linear correlation coefficient was r = 0.998. The calibration graph for accumulation time of 90 s was linear in the range from 2 × 10^{-9} mol L^{-1} to 2 × 10^{-7} mol L^{-1} and obeyed the equation y = 77.43x + 0.35, where y and x are the peak current (μA) and In(III) concentration (μmol L^{-1}), respectively. In this case the linear correlation coefficient was r = 0.996.

Detection limit

The detection limit estimated from a three-fold standard deviation for the lowest indium concentration and accumulation time of 60 s was equal to about 1.6 × 10^{-9} mol L^{-1} and for 90 s it was about 8.4 × 10^{-10} mol L^{-1}. **A comparison of detection limit, accumulation time, complexing agent and type of the working electrode used in this work with other ASV and AdSV procedures of In(III) determination are shown in Table 1.**

Precision

In order to assess precision of the procedure the parameters of repeatability and reproducibility were examined. For experiments the samples containing 1 × 10^{-8}, 5 × 10^{-8} and 1 × 10^{-7} mol L^{-1} In(III) standards were prepared. The repeatability

Table 1. The comparison of the present work to other ASV and AdSV procedures of In(III) determination.

Method	Complexing agent	Working electrode	Detection limit [mol L^{-1}]	Accumulation time [s]	Reference
ASV	**-**	**HMDE/MFE**	**1 × 10^{-8}**	**80**	**7**
	-	**HMDE**	**NI**	**120**	**8**
	-	**HMDE**	**3 × 10^{-7}**	**0**	**10**
	-	**HMDE**	**8.7 × 10^{-5}**	**300**	**11**
	-	**HgBiFE**	**1.45 × 10^{-7}**	**90**	**12**
	-	**BiFE**	**NI**	**60**	**13**
	-	**SbFE**	**1.22 × 10^{-8}**	**120**	**14**
	-	**SbFE**	**7 × 10^{-8}**	**NI**	**15**
	-	**SbFE**	**2.09 × 10^{-8}**	**120**	**16**
AdSV	**morin**	**HMDE**	**4 × 10^{-10}**	**300**	**17**
	xylenol orange	**HMDE**	**2.6 × 10^{-10}**	**60**	**18**
	APDC	**HMDE**	**1.3 × 10^{-9}**	**600**	**19**
	cupferron	**Hg(Ag)FE**	**1.5 × 10^{-10}**	**30**	**20**
	cupferron	**BiFE**	**1.6 × 10^{-9}**	**60**	**this work**
	cupferron	**BiFE**	**8.4 × 10^{-10}**	**90**	**this work**

NI – no information
HMDE – hanging mercury drop electrode
Hg(Ag)FE – mercury film silver based electrode
MFE – mercury film electrode
HgBiFE – mercury-bismuth film electrode
BiFE – bismuth film electrode
SbFE – antimony film electrode

of the measurements was evaluated from eight subsequent voltammetric measurements using different independent solutions as relative standard deviations (RSD) of the highest peak values and were equal to 3.7 %, 3.2 % and 2.6 % for each concentration. The reproducibility was evaluated from the measurements performed on five subsequent days as RSD and was equal to 3.8 %, 3.5 % and 3.0 %, respectively for each concentration.

Ruggedness and robustness

The ruggedness was evaluated as a measure of reproducibility of test results obtained by two analysts at the same laboratory and did not exceed 3.3 %.

The robustness was examined while the parameters such as the pH and buffer concentrations were slightly changed. We found that the obtained results did not change when those parameters were modified.

3.7. Study of interferences

It is well known that the analytical signal in adsorptive voltammetric methods is disturbed in the presence of different organic compounds which can be adsorbed on the electrode surface. The most common organic substances present in natural water are surfactants and humic substances. First the influence of surface active substances on the analytical signal of indium in the proposed procedure was studied. All kinds of surfactants such as cationic (CTAB), nonionic (Triton X-100), anionic (SDS) and biosurfactant (rhamnolipids) were examined. The measurements were carried out in solution containing a fixed concentration of In(III) equal to 1×10^{-7} mol L^{-1} and were performed using the standard procedure. Exploring the effects of different concentrations each of those surfactants was added to the sample in the range from 0.1 ppm to 20 ppm. It was observed that Triton X-100 and CTAB were the major sources of interferences. They caused total decay of the indium peak at a concentration of 0.5 ppm while rhamnolipids caused total decay of this signal at a concentration of 2 ppm. The anionic surfactant at a concentration of 20 ppm caused a decrease of the In(III) peak by about 30 %.

In order to eliminate the influence of surfactants the adsorptive properties of polymeric Amberlite XAD-7 resin were exploited. In earlier procedures for the determination of different metal ions it was proven that a simple, cheap and fast way to remove those effects of surfactants was previous mixing of the analyzed sample with resin.[21,38,42,43] **During mixing the solution organic compounds adsorbed on the resin while the analyte remained in solution. Thanks to this the determination could be carried out without the influence of interferents.** The measurements were performed as follows: 10 mL of the analyzed sample of indium, acetate buffer and one of the interferents was mixed with 0.5 g resin for 5 min. After sedimentation of the resin, 5 mL of the solution was pipetted into the voltammetric cell and next 0.5 mL of 1 mol L^{-1} acetate buffer at pH = 4.5, 800 µL of 1 g L^{-1} Bi(III), 100 µL of 1×10^{-2} cupferron and 3.6 mL of triply distilled water were added and the measurement was performed. Owing to the preliminary mixing with resin we were able to obtain an undisturbed signal of indium even in the presence of 20 ppm Triton X-100, CTAB and rhamnolipids. In the case of SDS this procedure allowed us to obtain an undisturbed signal up to the concentration of 50 ppm of anionic surfactant. **A comparison of the influence of Triton X-100, CTAB and SDS concentration on the voltammetric signal of 1×10^{-7} mol L^{-1} In(III) in the absence and in the presence of mixing with Amberlite XAD-7 resin is illustrated in Figure 4.**

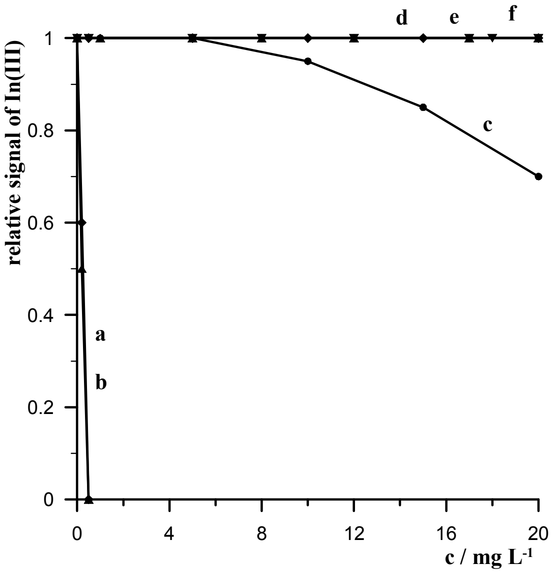

Figure 4. The influence of Triton X-100 (a, d), CTAB (b, e) and SDS (c, f) concentration on respective signals of 1×10^{-7} mol L^{-1} In(III). The measurements were carried out in the absence (a, b, c) and in the presence (d, e, f) of mixing with Amberlite XAD-7 resin.

The influence of commercially available organic matter was also examined. As the representatives of humic substances were selected: humic acids (HA), fulvic acids (FA) and natural organic matter (NOM). The measurements were carried out similarly as before. Surprisingly enough, none of those substances significantly affected the peak current of indium. An addition of 15 ppm of FA caused a decrease of the indium peak by about 30 % whereas 10 ppm FA, 15 ppm HA and 15 ppm NOM did not disturb the indium peak at all. As can be seen, the small impact of humic substances is greatest advantage of the described procedure. As compared with the earlier investigation of indium determination on the Hg(Ag)FE electrode,[20] 6 ppm FA, 4 ppm HA and 3 ppm NOM caused total decay of the indium signal. In view of the fact that in the present study the above effect **occurred to be** very small, it was not necessary to remove the interfering substances before the measurement. This allows a direct determination of indium trace in environmental water samples that may contain high concentrations of humic substances. In other words, there is no need to apply an additional step of mixing the solution with resin, **which was essential when the Hg(Ag)FE[20] was used instead of BiFE.**

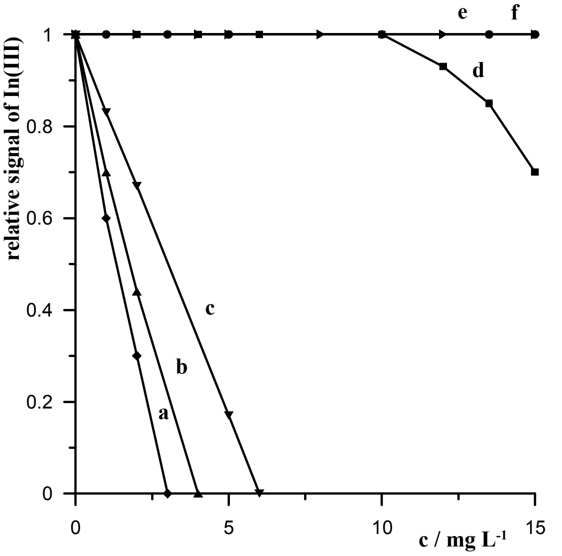

Figure 5. The influence of NOM (a, e), HA (b, f) and FA (c, d) concentration on the respective signal of 1 × 10^{-7} mol L^{-1} In(III). All measurements were carried out in the absence of mixing with Amberlite XAD-7 resin using Hg(Ag)FE[20] (a, b, c) and BiFE (d, e, f) as the working electrode.

3.8. Effect of foreign ions and EDTA

In the adsorptive voltammetric procedures, interferences of foreign ions can occur. These elements and their compounds can be adsorbed on the surface of the BiFE and prevent the accumulation of In(III)-cupferron complexes. The effects of foreign ions were tested using different concentrations of the examined ions and constant concentration of In(III) equal to 1 × 10^{-7} mol L^{-1}. The obtained results are presented as a tolerable limit of foreign ions, which means that the amount of ions that produced an error did not exceed 5 % in the peak current of indium. It was found that at least 1 × 10^{-5} mol L^{-1} of Cu(II), As(III), Fe(III), Cr(III), Cr(VI), Co(II), Zn(II), Ca(II), Mn(II), Mg(II), Ni(II), Al(III), Na(II), K(II), Pb(II), Hg(II), Ge(IV), Cd(II), Tl(I), 5 × 10^{-6} mol L^{-1} Sb(III), 2 × 10^{-6} mol L^{-1} As(V), W(VI) and 1 × 10^{-6} mol L^{-1} of Pd(II), Mo(VI), Se(IV) did not interfere. The 1 × 10^{-7} mol L^{-1} of Ti(IV) and 5 × 10^{-7} mol L^{-1} of Sn(II) caused total decay of the In(III) signal. A 10-fold excess of the V(V) and Ga(III) caused a decrease of the indium peak current to about 80 % whereas a 5-fold excess of the Pt(IV) and Au(III) caused a decrease of the indium signal to about 30 % and 45 %, respectively, as compared with the peak current recorded in the absence of foreign ions. **It should be noted that the classic foreign ions interferents of In(III) are Cd(II), Pb(II) and Tl(I). When these elements are incorporated, overlapping peaks are observed using mercury electrode.[44] A significant advantage of the proposed procedure where bismuth film electrode was adopted is the fact that even a 100-fold increase of Cd(II), Pb(II) and Tl(I) to In(II) does not influence the voltammetric peak of indium. The voltammograms recorded for solutions containing only In(III) and in the presence of the mentioned ions are presented in Figure 6. As can be seen, only in the presence of Pb(II) one additional peak was observed in the studied potential range, but it was well separated and it did not affect the In(III) signal.**

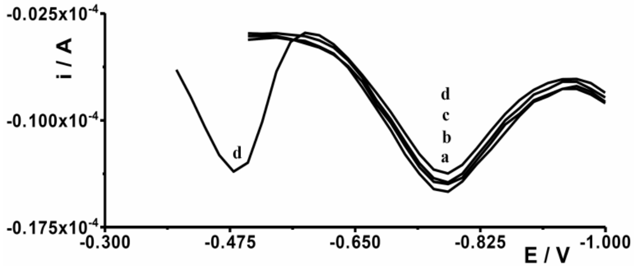

Figure 6. Differential pulse voltammograms recorded for solutions containing: 1 × 10^{-7} mol L^{-1} In(III) (b); as (b) + 1 × 10^{-5} mol L^{-1} Cd(II) (a); as (b) + 1 × 10^{-5} mol L^{-1} Tl(I) (c); as (b) + 1 × 10^{-5} mol L^{-1} Pb(II) (d).

The effect of EDTA was also studied. EDTA is a complexing agent whose maximum concentration present in wastewater, according to the information presented by World Health Organization (WHO), is 2 × 10^{-7} mol L^{-1}.[45] It was found that the addition of 2 × 10^{-7} mol L^{-1} and higher concentrations up to 1 × 10^{-5} mol L^{-1} did not affect the indium peak current. When the concentrations above 2 × 10^{-5} mol L^{-1} were added a slight decrease of the indium signal was observed. Thus is was concluded that the determination of In(III) can be performed even in wastewater containing a complexing agent.

3.9. Analysis of water samples

Using the optimum conditions the proposed method was examined for In(III) determination in water samples. The samples were collected from the Bystrzyca River and Lake Zemborzyce (eastern part of Poland) and stored in polypropylene bottles at the temperature of 6 °C. The voltammograms recorded for those samples did not exhibit any signals of In(III), so spiked experiments were performed. To confirm the possibility of using the proposed method in environmental water samples rich in humic substances, the Bystrzyca River and Lake Zemborzyce water samples spiked with indium and HA or FA or NOM were analyzed. The results obtained are presented in Table 2. The obtained results proved that the proposed method was sufficiently satisfactory for the analysis of real water samples. Figure 7 shows typical voltammograms obtained during the quantification in the spiked Lake Zemborzyce water.

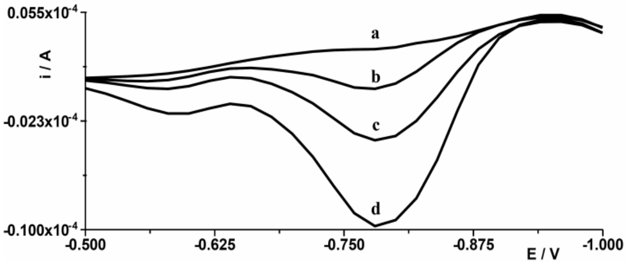

Figure 7. Differential pulse voltammograms obtained in the course of In(III) determination in Lake Zemborzyce: diluted five-fold (a); as (a) + 5 × 10^{-8} mol L^{-1} In(III) (b); as (a) + 1 × 10^{-7} mol L^{-1} In(III) (c); as (a) + 2 × 10^{-7} mol L^{-1} In(III) (d).

Table 2. Results of In(III) determination in water samples spiked with constant concentration of 1 × 10^{-7} mol L^{-1} In(III) and different concentrations of humic substances. In brackets the relative standard deviations in % are given (n = 3).

Water sample	Concentration of added humic substances [mg L^{-1}]			In(III) determined [1 × 10^{-7} mol L^{-1}]
	HA	FA	NOM	
Lake Zemborzyce	-	-	-	1.08 (4.7)
	10	-	-	0.97 (5.2)
	-	5	-	0.93 (3.7)
	-	-	5	0.95 (6.1)
Bystrzyca river water	-	-	-	1.06 (4.6)
	10	-	-	1.02 (3.8)
	-	5	-	0.92 (6.1)
	-	-	5	0.97 (6.4)

Conclusions

The AdSV determination of indium with cupferron as a complexing agent and in situ plated bismuth film electrode is a very satisfactory proposition for analysis of water samples. The main advantages of this electrode are the possibility of formation in situ from the solution and lower toxicity as compared with mercury electrodes. The proposed procedure leads to a shortening of the time of measurement and also it is simple, fast and cheap as there is no need to use expensive equipment. The determination of metal traces in environmental water samples using AdSV methods is normally difficult when humic substances are present. In the proposed procedure, it was found that humic substances and the majority of foreign ions did not cause interferences. This is a great advantage in comparison with other techniques which employed mercury electrodes as a working electrode. The described method allows one to carry out the analysis without necessary elimination of organic substances. The successful practical application of the proposed method for the direct determination of indium in natural water samples appears to be promising for use in environmental measurements.

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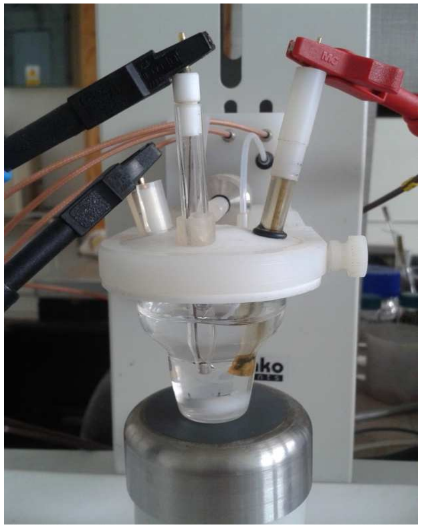
In(III)-kupferron



BiFE

AdSV