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CPST INSTITUTE OF CHEMISTRY

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INVESTIGATION OF HEAVY METAL DETERMINATION USING ELECTROANALYTICAL STRIPPING ANALYSIS

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VILNIAUS UNIVERSITETAS
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SUNKIŲJŲ METALŲ INVERSINIO ELEKTROANALIZINIO NUSTATYMO TYRIMAI

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1. INTRODUCTION

Electroanalytical techniques are concerned with the interplay between electricity and chemistry, namely the measurements of electrical quantities, such as current, potential, or charge, and their relationship to chemical parameters. Such use of electrical measurements for analytical purposes has found a vast range of applications, including environmental monitoring, industrial quality control and biomedical analysis. Advances in the 1980s and 1990s – including the development of ultra-microelectrodes, the development of ultratrace voltammetric techniques or high – resolution scanning probe microscopies have led to a substantial increase in the popularity of electroanalysis and to expansion into new phases and environments for heavy metals determination.

Electrochemical stripping analysis is still recognized as one of the most convenient techniques for measuring trace heavy metal ions, in particular due to its capability of pre – concentrating analytes at/in the surface of the working electrode. For these purpose, a great variety of electrode materials have been reported, such as gold, platinum, silver, mercury, iridium, several alloys and amalgams. Among them, mercury based electrodes have been mostly used in the last five decades due to superior electroanalytical performance of mercury over other candidates. However despite the excellent performance of mercury electrodes, future regulations and occupational health considerations may severely restrict or even ban the use of mercury as an electrode material because of its high toxicity.

New alternative electrode materials are then highly desired to develop “environmentally friendly” stripping sensors suitable for on-site heavy metals monitoring. Numerous solid electrode materials, including gold, carbon – based or iridium have been tested, but overall performance has never approached those of mercury. Since Wang’s research group reported the first use of bismuth film electrode, the use of bismuth film electrodes has been the focus of a number of studies with analytical applications centred on the detection of heavy metals. Bismuth film electrode was introduced as a favorable replacement for mercury electrodes. Also antimony, as a metal related to bismuth, has its history in electrochemistry. Another metal, which is related to bismuth and can form intermetallic compounds with other metals is gallium.

Gallium film electrode also could be a good replacement for mercury electrodes but more studies have to be done.

The aim of the work is to investigate gallium and bismuth film plating *in situ* and *ex situ* processes as well as to optimize metal film plating conditions for determination of heavy metals in water samples.

The main tasks set to achieve the aim were as follows:

1. To investigate electrochemical and microscopic properties of the bismuth film electrode.
2. To apply bismuth film electrode for determination of heavy metals in water samples.
3. To investigate gallium film plating on carbon paste and glassy carbon substrates.
4. To optimize gallium film plating conditions.
5. To apply gallium film electrode for determination of heavy metals in water samples.

Novelty and actuality of the work

With the development of industry and technology, the growth in consumption of environmental resources rises heavily, while there is also the problem of various wastes containing heavy metals. It is important to monitor heavy metals in various systems. This work investigates bismuth and gallium film electrodes as an alternative tool for determination of heavy metals in water samples. Industrially gallium and bismuth are considered one of the less toxic of the heavy metals, but have not been studied enough for suitability for determination of heavy metals. Especially, there are no many investigations of gallium film electrodes. The electrochemical and microscopic properties of bismuth film electrode were investigated. It has been shown that bismuth film electrode can be used for determination of heavy metals. Gallium film plating conditions were optimized on glassy carbon substrate. Gallium influence on Pb(II) and Cd(II) deposition was studied. It has been shown that gallium film plated *in situ* and preferably onto the carbon paste-based support can be employed as a detection tool in anodic stripping voltammetry of Zn(II) at the trace concentration level.

2. EXPERIMENTAL

2.1. Chemicals and solutions

Bismuth(III) nitrate, gallium(III) nitrate, lead(II) acetate, cadmium(II) nitrate, and zinc(II) acetate were obtained from Sigma (Germany) of analytical grade. Stock solutions of the salts mentioned above, concentration 1 g L^{-1}, were prepared in acetate buffer and stored at room temperature. They were diluted as required before measurements. Two main stock solutions of acetate buffer (AcB; equimolar mixture of CH_3COOH + CH_3COONa) and hydrochloric acid were made 0.1 M in concentration. Other solutions, including some complex-forming media, were $HClO_4$, NaOH, ammonia and phosphate buffers (0.5 mol L^{-1}), KCl, KBr and citrate (0.1 mol L^{-1}), plus EDTA (0.01 mol L^{-1}). All the solutions were made from doubly deionised water.

2.2. Instruments and methods

A three-electrode cell was used for voltammetric measurements, containing a glassy carbon disk (2 mm in diameter) or carbon paste disk (2 mm in diameter) working electrode, a platinum foil counter electrode and an Ag/AgCl (3 M NaCl) electrode as reference. All potentials below are given versus this reference. Square wave and cyclic voltammetry measurements were performed using a computer-controlled PalmSens potentiostat with PSTrace 3.0 software (PalmSens, Netherlands). For square wave anodic stripping voltammetry (SWASV) the frequency was 25 Hz, step potential 5 mV, amplitude 25 mV and equilibration time 15 s. Measurements of pH were achieved using a Mettler Toledo MP 220 pH-meter and a Mettler Toledo InLab 410 glass electrode, which was calibrated with the standard buffer solutions in the pH range from 4.01 to 6.98. The surfaces of the samples were examined using an EVO 50EP (Carl Zeiss SMT AG, Germany) scanning electron microscope. All observations were carried out with a secondary electron (SE) detector in high-vacuum mode at 30 kV accelerating voltage.

2.3. Bi film formation

Glassy carbon electrode was polished with Al_2O_3 slurry with the particle size of 1, 0.3 and 0.05 µm (Micropolish II, Buehler, USA) using a polishing pad (Microcloth, Buehler, USA); each polishing step followed sonication in water for 3 min. Bismuth films were formed by deposition onto the glassy carbon electrode at constant applied potential. Films were deposited from the solutions containing different concentrations of Bi(III) in 0.1 M acetate buffer, pH 4.5 in the presence and absence of KBr. The electrode was previously held at +0.3 V for 5 min to reoxidize any heavy metal species present at the electrode surface and the solution was stirred during conditioning and deposition. Films were either predeposited ex situ in a different solution from that used for characterization or for measurement of trace metals or in situ together with the other metal ions.

2.4. Ga film formation

Gallium films were deposited *in situ*; it means by potentiostatic electrolysis performed directly in sample solutions with Ga^{3+} ions. The carbon paste surface was renewed mechanically by its smoothing with a wet filter paper and this operation was usually made prior to each new set of measurements. The glassy carbon surface was renewed by electrochemical cleaning / conditioning at +0.3 V vs. ref for 5 min. and, if needed, with previous polishing. Films were deposited from a solution containing 1 mg L^{-1}, 5 mg L^{-1} and 10 mg L^{-1} Bi(III) in different buffers. Typical experiments comprised a pre-concentration step at −1.70 V vs. ref., followed by a 15 s equilibration period with a pre-concentration time of 60 or 120 s. The SWV-modulation ramp was set as follows: pulse amplitude, ΔE_{SW} = +50 mV; frequency, f_{SW} = 25 kHz; the potential increment, i_{SW} = 5 mV. Some parameters could slightly be varied and therefore, the actual values are always specified in the legend of each figure presented.

2.5. Voltammetric measurements

The concentrations of Zn(II), Cd(II), Cu(II) and Pb(II) in solutions were determined by the anodic stripping voltammetry using bismuth film and gallium film electrodes. The linear calibration curve of each metal was obtained from square wave anodic stripping voltammetry measurements with increasing concentrations of Zn(II), Cd(II), Cu(II) and Pb(II) in the acetate buffer (pH 4.5). Zn(II), Cd(II), Cu(II) and Pb(II) ions were determined in the water samples by means of the standard addition method. 5 µL of investigative water sample was added to the 10 ml cell, containing 0.1 M of acetate buffer and 500 µg L^{-1} of Bi(III) or 1 mg L^{-1} of Ga(III), after recording the background voltammogram.

3. RESULTS AND DISCUSSION

3.1. Microscopic investigation of the Bi film electrode

Bi film first was deposited on polished and preconditioned glassy carbon electrode. Bi film deposited without bromide from 2 mg L^{-1} (9.6 µmol L^{-1}) solution of Bi(III) in acetate buffer pH 4.5, the film obtained was not uniform and Bi aggregates randomly spread on the electrode surface and the bare glassy carbon was still visible (not shown). After Br^- addition to the deposition solution, a compact film was deposited as seen from Figure 1a. However, this film with Br^- addition was not perfectly uniform and not smooth (Fig. 1a), it is formed from separated crystals those grow together and form complex aggregates where instead of bromide Bi(III) was complexed with citrate. The edges of the aggregates, with the different size but not bigger than 300 nm, were randomly distributed on the electrode surface. In order to follow the structure of intermetallic compounds that Bi forms with the other metals, films were deposited in situ with Cd and/or Pb. Figures 1b, c represent a surface structure of Bi film co-deposited together with Cd at different magnifications. This film was deposited from a solution containing 2 mg L^{-1} of Bi(III) and 0.5 mg L^{-1} (4.5 µmol L^{-1}) of Cd(II) and 0.1 M KBr for 600 s. The film was solid on the electrode surface, but the aggregates had a totally different shape as compared with Bi film without Cd. Bi-Cd film formed the aggregates of various sizes and they were random distributed on the electrode surface. The size of the aggregates varied from hundred to several hundred nanometers and their distribution density was random. The shape of aggregates varied and no clear tendency has been found. This demonstrates that Bi and Cd definitely form intermetallic alloy, which has not uniform structure and is completely different from Bi film. Since the concentration of Cd was lower than Bi(III) it is hardly to expect that Cd structure was predominant. It seems that film grew from separate active centers. The aggregates size and distribution are not uniform, which was easy to observe at higher magnification (Fig. 1c).

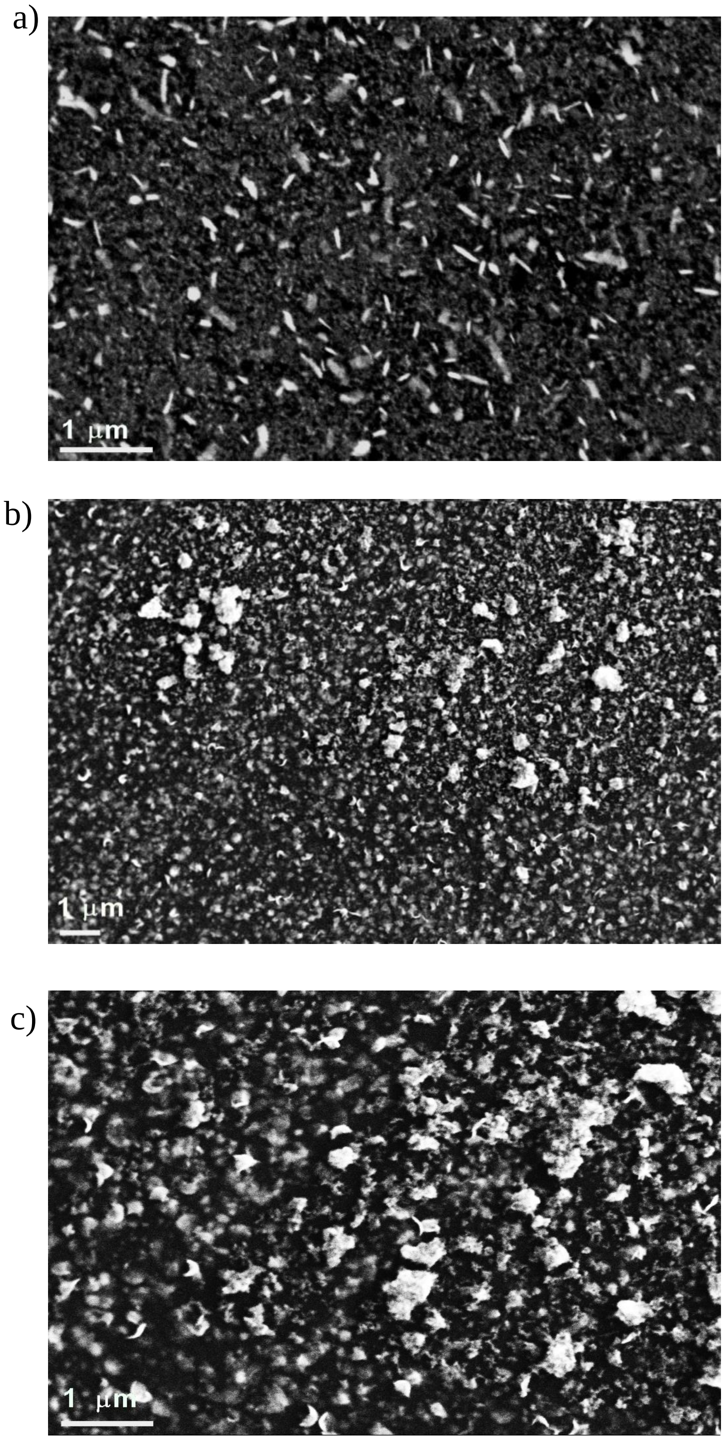

Figure 1. SEM images of Bi film, deposited from solution containing 2 mg L^{-1} Bi(III), 0.1 M KBr, 0.1 M acetate buffer pH 4.5 (a), and Bi-Cd film, deposited from solution containing 2 mg L^{-1} Bi(III), 0.5 mg L^{-1} Cd(II), 0.1 M KBr, 0.1 M acetate buffer pH 4.5 (b and c the same surface at different magnifications).

The other metal quite often used for determination at BiFE is Pb. So, Bi film was deposited together with Pb as well applying the same conditions like in the case of Bi or Bi-Cd film, keeping the same concentration ratio, i.e. 2 mg L^{-1} of Bi(III) and 0.5 mg L^{-1} (2.4 µmol L^{-1}) of Pb(II) and 0.1 M KBr, with the aim to see whereas Bi-Cd and Bi-Pb films are similar. The SEM images of the resulting film are presented in Figure 2. Likewise in this case, solid but not uniform film, containing crystal aggregates, has been obtained. The shape of the aggregates was different from both Bi and Bi-Cd films. The edges of the aggregates, with the size between 100 and 200 nm, were randomly distributed on the electrode surface and they had rather a regular shape, moreover, their density on surface area was quite uniform, which is clearly visible at both lower (Fig. 2a) and higher (Fig. 2b) magnifications. From the form of the aggregates and their distribution it seems that Bi and Pb easier form intermetallic compounds than Bi and Cd.

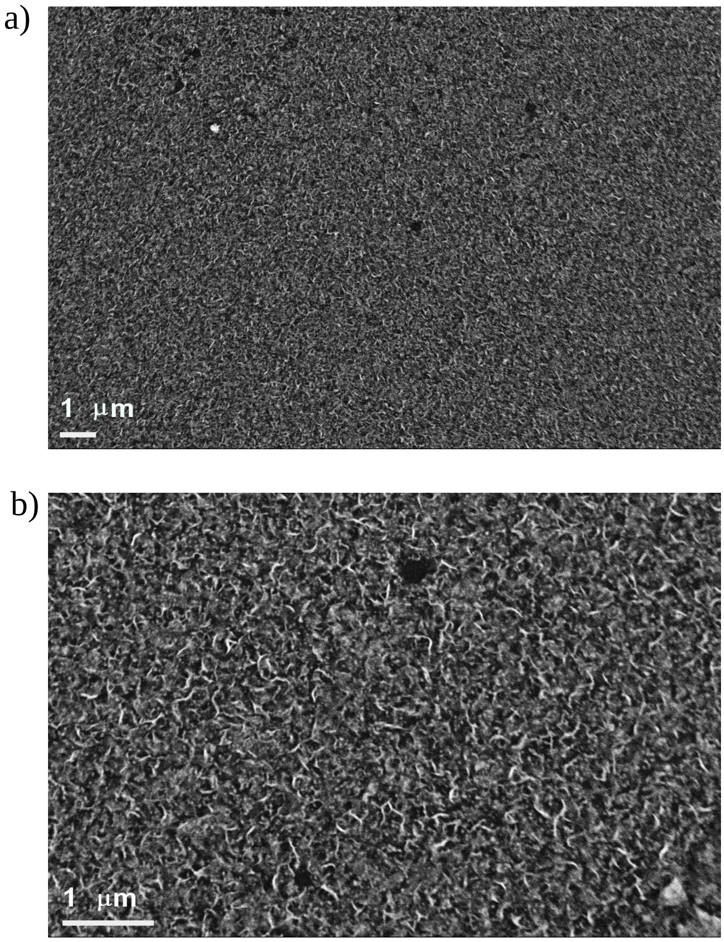

Figure 2. SEM images of Bi-Pb film, deposited from solution containing 2 mg L^{-1} Bi(III), 0.5 mg L^{-1} Pb(II), 0.1 M KBr, and 0.1 M acetate buffer pH 4.5 (a and b the same surface at different magnifications).

In order to study if multimetallic complexes are just mixture of bimetallic compounds or alloy of all of them, Bi film was deposited together with Cd and Pb simultaneously. The result obtained by SEM was rather surprising and presented in Fig. 3. The film was not uniform and the crystallization centers at the defects at the electrode surface, introduced by polishing, are clearly visible at lower magnification (Fig. 3a). The nanosize crystals were obtained with rather a regular shape and a similar size, which was around 30 – 50 nm (Fig. 3b). Surprisingly, these crystals did not grow together to the aggregates, and even during the deposition time of 600 s the electrode surface was not fully covered.

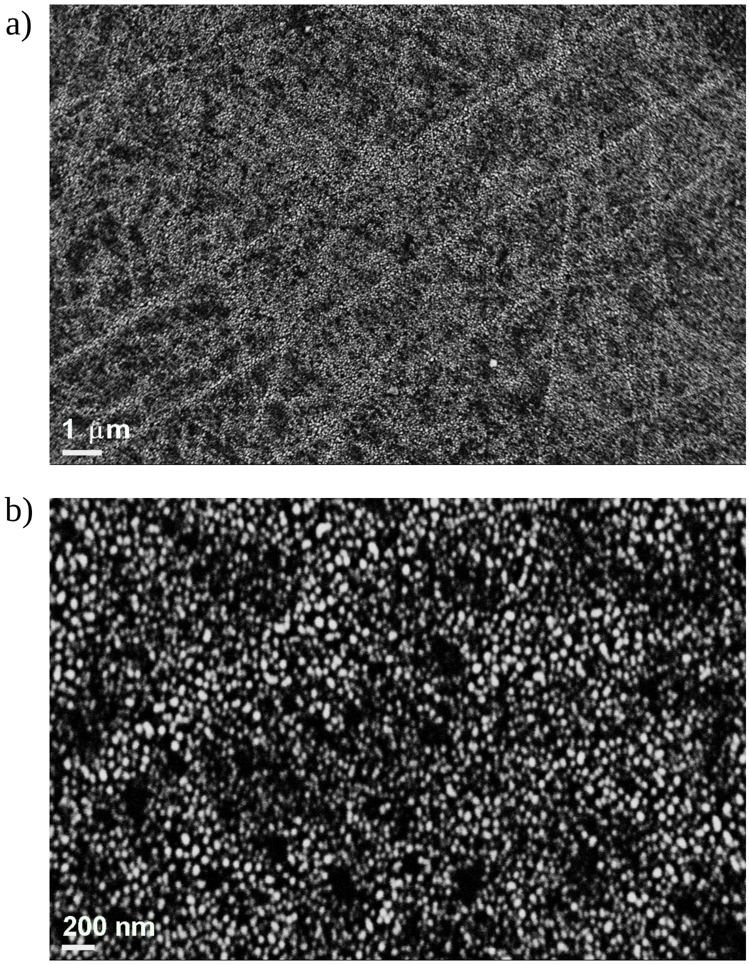

Figure 3. SEM images of Bi-Cd-Pb film, deposited from solution containing 2 mg L^{-1} Bi(III), 0.5 mg L^{-1} Cd(II), 0.5 mg L^{-1} Pb(II), 0.1 M KBr, and 0.1 M acetate buffer pH 4.5 (a and b the same surface at different magnifications).

3.2. Electrochemical characterization of the Bi films

3.2.1. Cyclic voltammetry

Cyclic voltammograms were recorded at BiFE with and without Cd and/or Pb. The films were deposited from the solutions described above at -1 V for 300 s and the voltammograms were then registered in the same solution. Figure 4 presents CVs at BiFE in absence (dashed line) and presence of KBr (solid line). The Bi dissolution peak was obtained at 0.0 V, and the peak height was 345 µA cm^{-2} in the forwards going scan, and the bismuth reduction started at -0.5 V and the limiting current density of -160 µA cm^{-2} was found at -0.74 V in the backwards going scan. When KBr was added to the deposition solution, the Bi dissolution peak was slightly shifted to negative potential, i.e. to -0.05 V, and the peak height was 1.8 times higher than without Br$^-$. Nevertheless, a second peak remained at -0.74 V as in the case without KBr. The first peak is reduction of $[BiBr_n]^{3-n}$ (n= 1 – 6) species, and the second one is direct Bi(III) reduction. However, no significant changes in reduction of Bi was observed in CVs with and without Br$^-$ using different Bi(III) salts in HCl electrolyte, showing that Bi also forms complex with Cl$^-$.

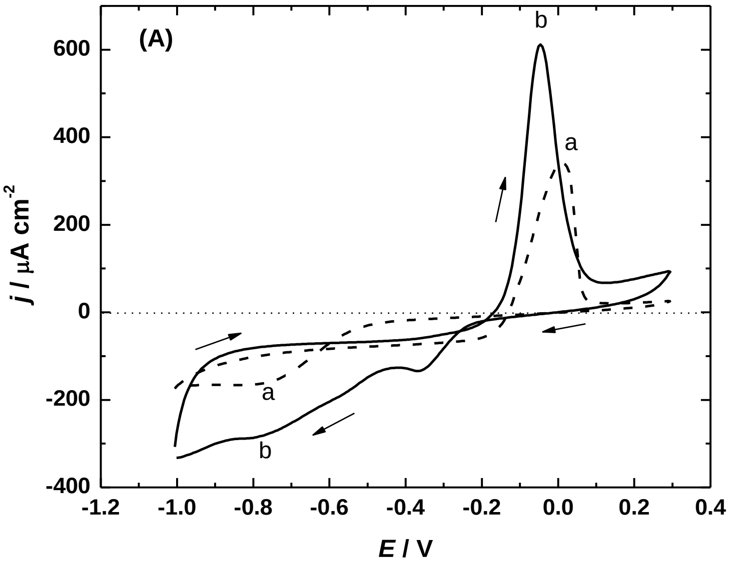

Figure 4. Cyclic voltammograms of Bi film deposited on glassy carbon electrode in presence (solid line) and in absence (dashed line) of KBr. Film deposited at -1 V for 300 s from solution containing 2 mg L^{-1} Bi(III), 0 or 0.1 M KBr, and 0.1 M acetate buffer pH 4.5.

3.2.2. Square wave anodic stripping voltammetry

The SWASVs were registered at BiFE with and without Cd and/or Pb. When investigating the Bi-Cd film, the Cd-peak was obtained at -0.75 V and the Bi-peak was slightly shifted to more negative potentials than without Cd, and it was observed at -0.08 V (Fig. 5, dashed line), showing that Bi stripping from Bi-Cd intermetallic structure is facilitated. However, rather low Cd peak was obtained, and the Bi peak was also lower than without Cd (Fig. 5, solid line). This fact shows that either the electrode surface is blocked somehow or Bi-Cd film is depositing much more slowly than the individual Bi film.

Much higher peaks were found when Pb was added to the deposition solution instead of Cd. The peaks were at -0.49 V (Pb) and at -0.10 V (Bi) as seen from Figure 5 (dotted line). The Bi peak was shifted again to more negative potentials, showing that Bi-Pb film is even easier to strip from the electrode surface. As it was suspected from SEM investigation (Fig. 2), Bi-Pb easier forms intermetallic structures catalyzing each other deposition. The SWASV results also confirmed this hypothesis since much higher peak was obtained for Pb although its molar concentration was almost twice lower than Cd (2.4 and 4.5 µM, respectively). It might also be that Pb film is dominating and Bi was co-deposited, since is known that Pb also can form intermetallic compounds and can be successfully applied as a film for the determination of other metals.

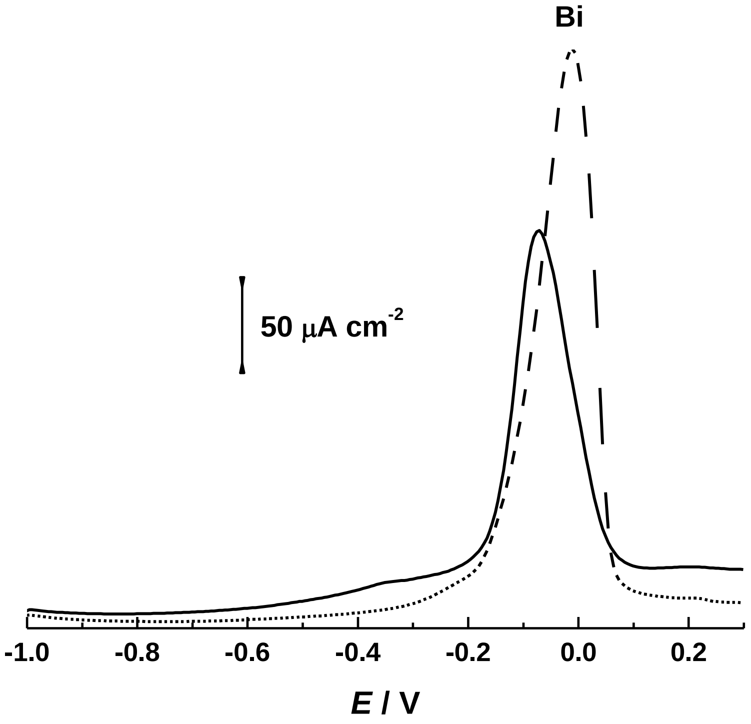

Figure 5. Square wave anodic stripping voltammograms of Bi-metal films deposited at -1 V for 120 s from solutions, containing 2 mg L_1 Bi(III), 0.1 M KBr, and 0.1 M acetate buffer pH 4.5 and either 0.5 mg L^{-1} Cd (dotted line) or 0.5 mg L^{-1} Pb (dashed line), or both 0.5 mg L^{-1} Cd and 0.5 mg L^{-1} Pb (solid line).

The film deposited from solution containing all 3 metal ions together formed Bi-Cd-Pb nanoparticle structure (Fig. 3), which SWASV profile is presented in Figure 5 (solid line) and it was similar to those of the individual Bi-Cd and Bi-Pb films. The peak positions were the same like in the individual films, i.e. -0.75, -0.49, and -0.1 V for Cd, Pb, and Bi respectively. Even in this case Pb peak was predominant either by peak height or by peak area. However, it is hardly possible to explain the formation of the nanoparticles in this case, since the peak position is neither shifted nor other evidence was found in the stripping voltammogram. It also might be that nanoparticles were formed due to rather high total concentration of the metal ions in the deposition solution.

3.3. Analysis of solutions

Concentrations of Zn(II), Pb(II), Cd(II) in solutions were determined by anodic stripping voltammetry with a bismuth film electrode (BFE). The deposition potential was selected in accordance to the target metals: for Zn(II) it was -1.3 V (preconcentration time 120 s), while for Cd(II), Cu(II), Pb(II) it was -1.2 V (preconcentration time 60 or

120 s). All measurements were carried out at room temperature in non-deaerated solutions. For square wave anodic stripping voltammetry (SWASV) the frequency was 25 Hz, step potential 5 mV, amplitude 25 mV and equilibration time 15 s. A 30 s conditioning step at +0.4 V was used to remove the target metals and bismuth films, prior to the next cycle.

The linear calibration curve of each metal was obtained from SWASV measurements with increasing concentrations of Zn(II), Cd(II), Cu(II) and Pb(II) in the acetate buffer (pH 4.5). Good linear responses of the peak area vs. concentration were obtained for Zn(II), Cd(II), Pb(II) and Cu (II) up to the concentration level of 150, 130, 90 and 100 µg L^{-1} and correlation coefficients of 0.997, 0.997, 0.999 and 0.998 respectively. An example of the determination of Cu(II), Pb(II) and Cd(II) ions in their mixture using the bismuth film electrode is presented in Fig. 6.

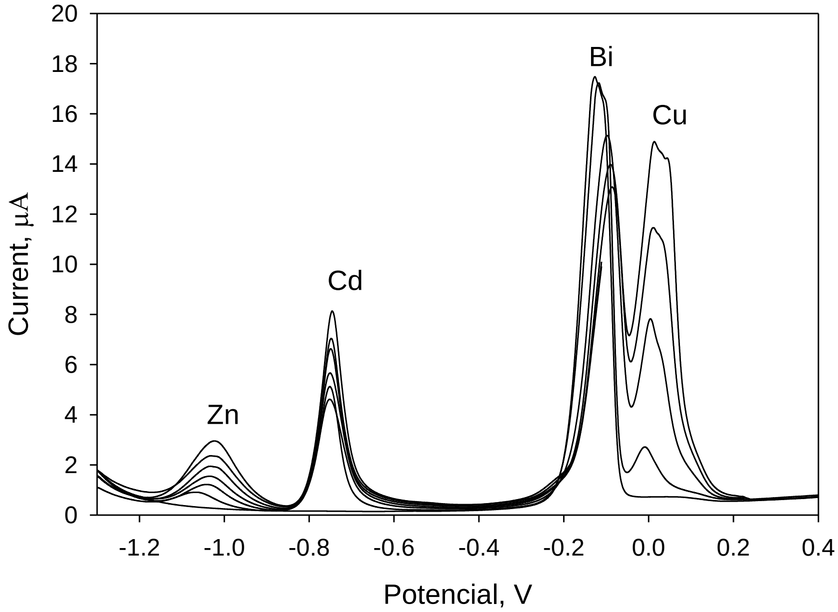

Figure 6. Series of voltammograms for increasing concentrations of Zn(II), Cd(II) and Cu(II) on in situ plated BFE in 0.1 mol L^{-1} acetate buffer (pH 4.5) with 500 µg L^{-1} Bi(III). Conditions: frequency 25 Hz, step potential 5 mV, amplitude 25 mV, equilibration 15 s, deposition for 120 s at -1.2 V, equilibration time 15 s and cleaning for 30 s at +0.4 V; from below: blank and successive additions of 10 µg L^{-1} of Zn(II), Cd(II) and Cu(II).

3.4. Optimization of experimental conditions of gallium film formation

Four parameters were optimized: concentration of Ga(III) ions in a plating solution, the potential of film formation, time of film formation and the temperature of film formation. The influence of temperature was observed on gallium film formation. As shown in Fig. 7 higher temperature gives better voltammetric response of gallium. Due to poor repeatability of gallium peaks at 50° C temperature, a 40° C temperature was chosen for further study.

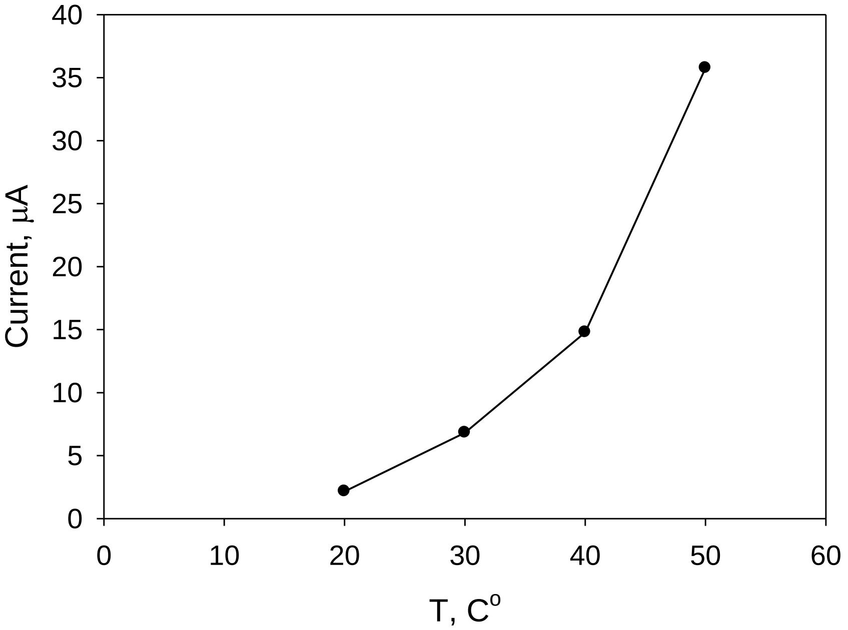

Figure 7. The influence of temperature on Ga(III) peak current. Solution: 0.1 mol L^{-1} acetate buffer (pH 4.5) containing 1 mg L^{-1} Ga(III). Deposition at -1.7 V for 120 s.

Voltammograms of concentration optimization are shown in Fig. 8. The optimum concentration for the deposition of the gallium film was found to be 1 mg L^{-1} Ga(III). This concentration of Ga(III) in the analyzed solution yielded the highest sensitivity and excellent resolution of gallium voltammetric response. For the concentration of 0.5 mg L^{-1} and 2 mg L^{-1} of Ga(III) the observed peaks are not well – shaped and have lower values.

The influence of the deposition potential on gallium film formation is presented in Fig. 9. For further study deposition potential of gallium film formation equal to -1.7 V was chosen. The influence of time on gallium film formation is shown in Fig. 10. For further study the time of film formation of 120 s was chosen.

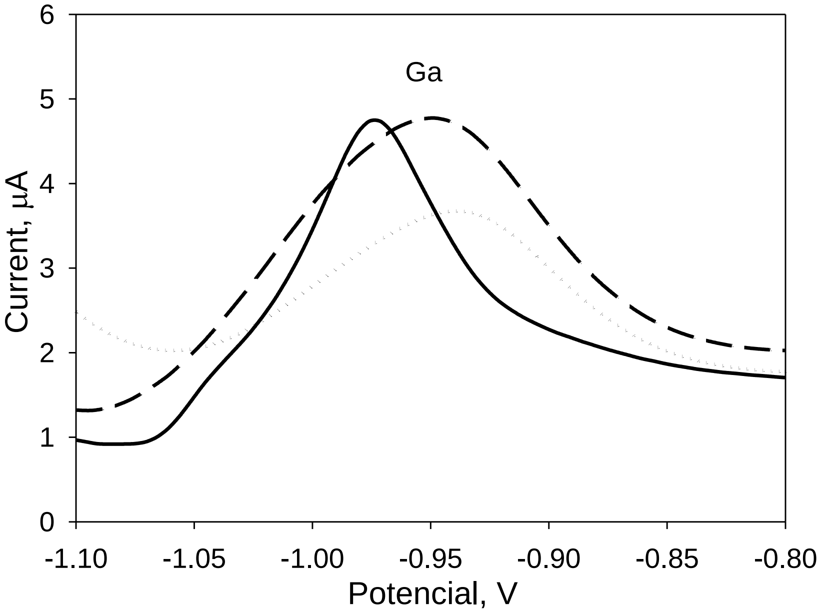

Figure 8. Square waves voltammograms for various Ga(III) concentrations. Solution: 0.1 mol L^{-1} acetate buffer (pH 4.5) containing 0.5 mg L^{-1} Ga(III) (dotted line), 1 mg L^{-1} Ga(III) (solid line), 2 mg L^{-1} Ga(III) (dashed line). Deposition potential -1.7 V, deposition time 120 s, deposition temperature 40° C.

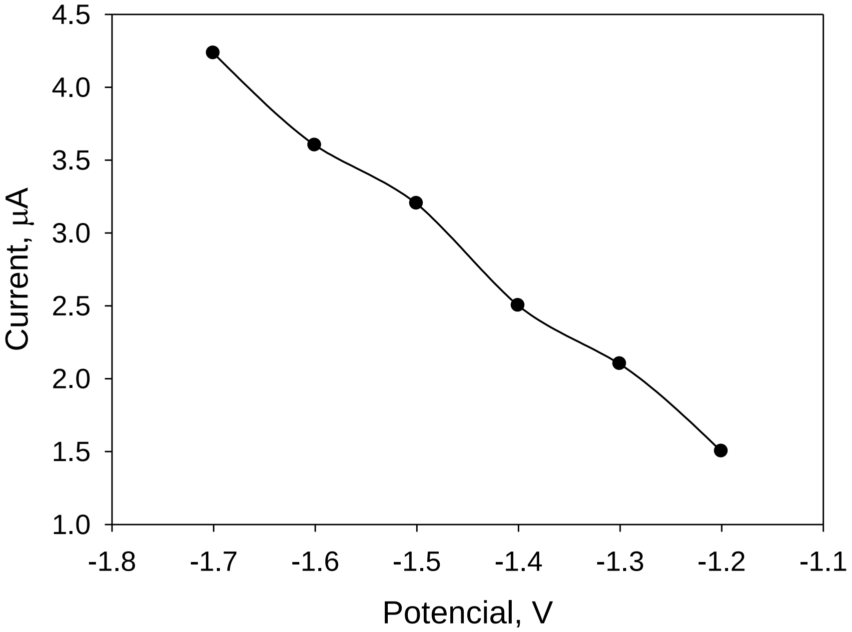

Figure 9. The influence of deposition potential on Ga(III) peak current. Solution: 0.1 mol L^{-1} acetate buffer (pH 4.5) containing 1 mg L^{-1} Ga(III). Deposition time 120 s, deposition temperature 40° C.

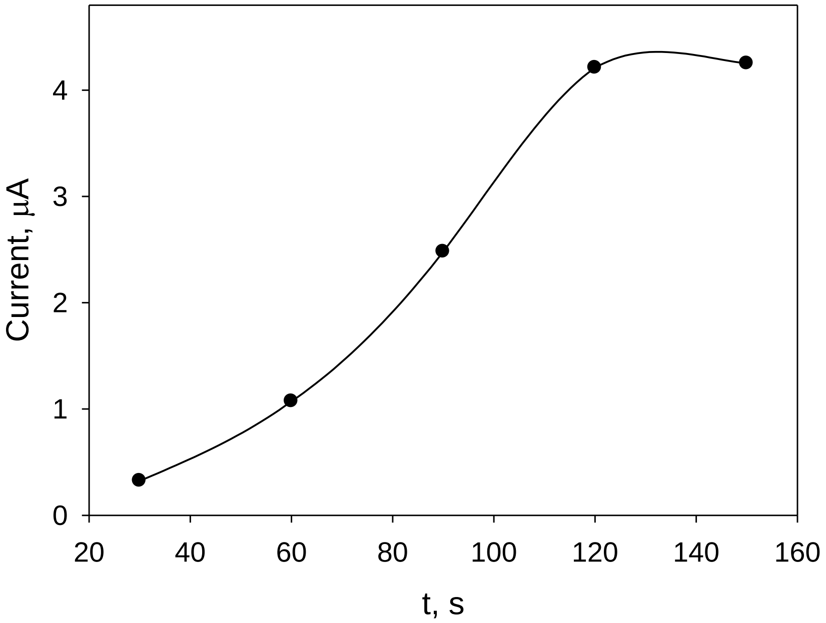

Figure 10. The influence of time on Ga(III) peak current. Solution: 0.1 mol L^{-1} acetate buffer (pH 4.5) containing 1 mg L^{-1} Ga(III). Deposition potential -1.7 V, deposition temperature 40^{o} C.

3.5. Ga(III) influence on Pb(II) and Cd(II) deposition

During the studies gallium influence on Pb(II) and Cd(II) deposition was observed. First, only 50 µg L^{-1} Pb(II) was deposited on the glassy carbon electrode in 0.1 M acetate buffer (pH=4.5). Then depositions of Pb(II) were made in solutions containing 1 mg L^{-1} Ga(III) using *in situ* and *ex situ* methods. Due to a possibility of hydrogen evolution process during the deposition a lower deposition potential of -1.5 V was chosen. Deposition time was 120 s. Voltammograms obtained from these studies are shown in **Fig. 11**. These results showed, that gallium ions have significant effect on Pb(II) deposition. Deposition of Pb(II) with additional Ga(III) ions gives well – shaped peak of Pb(II) (solid line) compare to the other studies when Pb(II) was not detected (dotted line, dashed line).

The same studies were performed with Cd(II). Obtained voltammograms are shown in **Fig. 12.** All measurements were performed under the same conditions as with Pb(II). Hence, the addition of gallium is having a major effect on the peak height of the cadmium signal (solid line). Cd(II) signal was not detected during the deposition with 1 mg L^{-1} Ga(III) using *ex situ* method (dotted line).

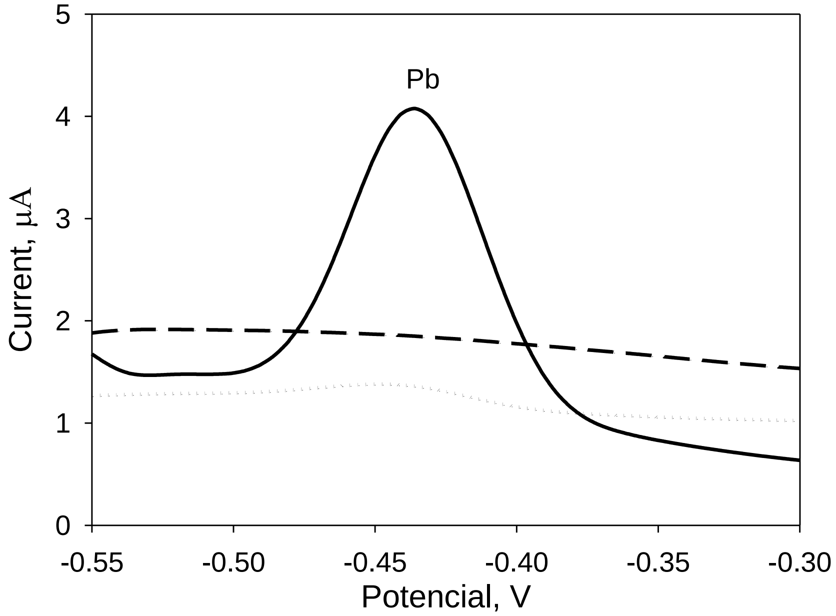

Figure 11. Square waves voltammograms for Pb(II) concentrations. 50 µg L^{-1} Pb(II) (dotted line), 1 mg L^{-1} Ga(III) and 50 µg L^{-1} Pb(II) *in situ* (solid line), 1 mg L^{-1} Ga(III) and 50 µg L^{-1} Pb(II) *ex situ* (dashed line). Deposition time 120 s, deposition potential -1.5 V, deposition temperature 40^o C. Supporting electrolyte 0.1 mol L^{-1} acetate buffer (pH 4.5).

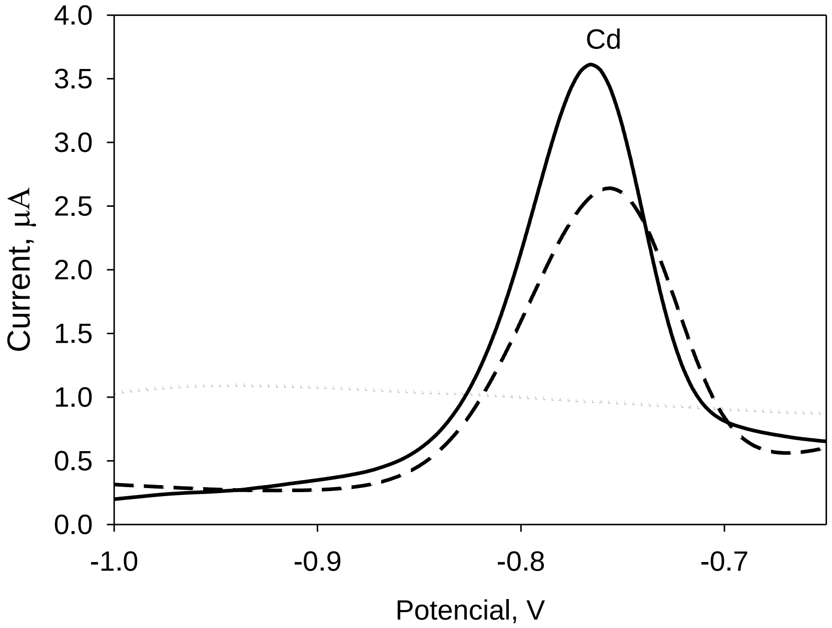

Figure 12. Square waves voltammograms for Cd(II) concentrations. 50 µg L^{-1} Cd(II) (dashed line), 1 mg L^{-1} Ga(III) and 50 µg L^{-1} Cd(II) *in situ* (solid line), 1 mg L^{-1} Ga(III) and 50 µg L^{-1} Cd(II) *ex situ* (dotted line). Deposition time 120 s, deposition potential -1.5 V, deposition temperature 40^o C. Supporting electrolyte 0.1 mol L^{-1} acetate buffer (pH 4.5).

3.6. Possibilities and limitations of the determination of Zinc(II) at gallium film electrodes

3.6.1. Gallium film formation at the glassy carbon and carbon paste electrodes

The corresponding assay has been carried out with two different carbon substrates, GCE and CPE, in a solution of 0.1 M acetate buffer taken as the model supporting electrolyte and with two different concentrations of 5 and 10 mg L^{-1} Ga(III) at room temperature. Due to a highly negative potential required for dissolution of gallium the deposition had always been performed at potentials more negative than –1.5 V vs. Ag/AgCl.

The proper dissolution process, *i.e.*, reoxidation $Ga^0 \rightarrow Ga^{III}$, is shown in **Fig. 13** and **Fig. 14**, making comparison of the performance of two different GaFEs operated *in situ* and prepared from two different substrates under the same conditions. All voltammograms confirm the functionality of both film electrodes, as well as somewhat better developed response of the GaF-CPE configuration, indicating somewhat better behaviour of the deposited film at the carbon paste-based substrate.

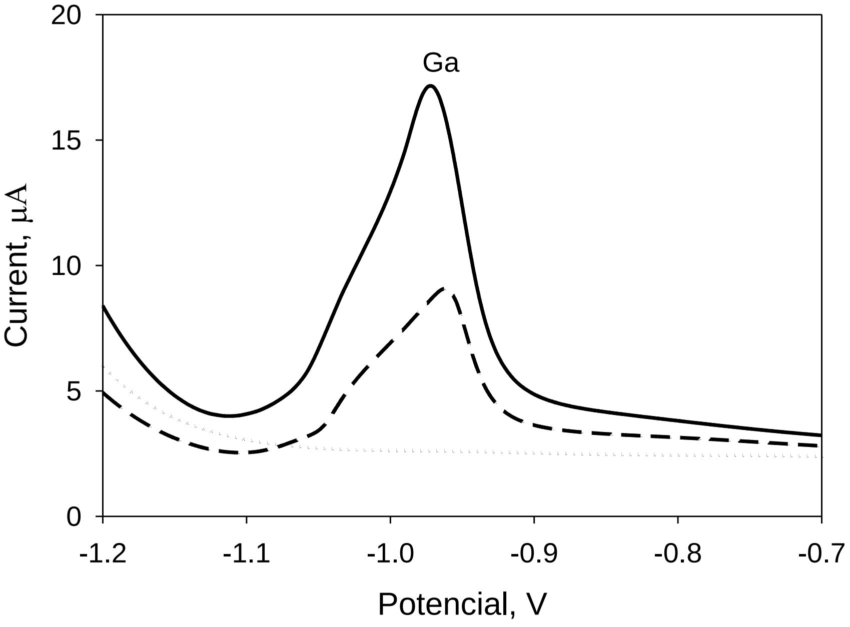

Figure 13. Square waves voltammograms for various Ga(III) concentrations at the glassy carbon substrate. Blank (dotted line), 5 mg L^{-1} (dashed line), 10 mg L^{-1} (solid line). Deposition time was 60 s, deposition potential -1.7 V. Supporting electrolyte 0.1 mol L^{-1} acetate buffer (pH 4.5).

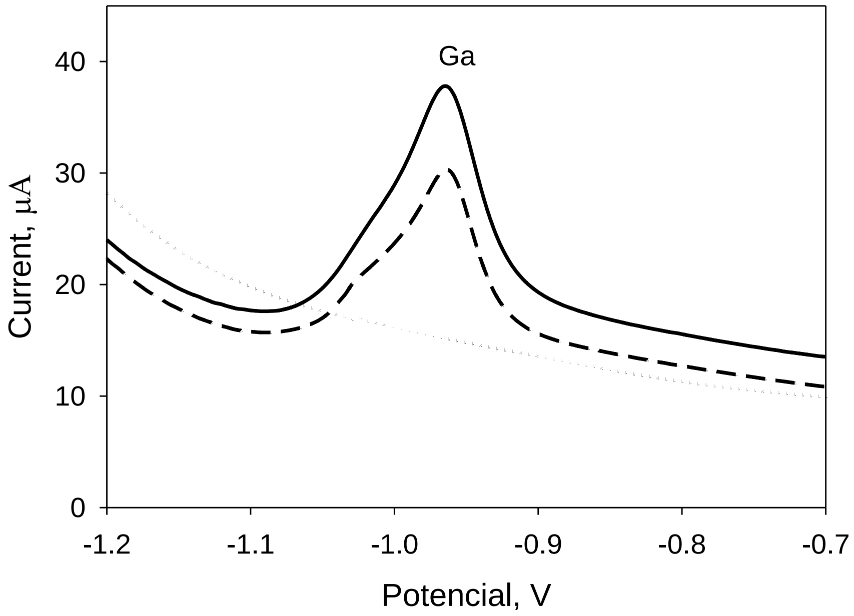

Figure 14. Square waves voltammograms for various Ga(III) concentrations at the carbon paste substrate. Blank (dotted line), 5 mg L^{-1} (dashed line), 10 mg L^{-1} (solid line). Deposition time was 60 s, deposition potential -1.7 V. Supporting electrolyte 0.1 mol L^{-1} acetate buffer (pH 4.5).

3.6.2. Anodic stripping voltammetry of Zn(II)

In anodic stripping voltammetry with common non-mercury electrodes, the determination of Zn(II) is less reliable compared to those applicable to Pb(II), Cd(II), or Cu(II). At first, there is lesser efficiency of the zinc deposition inevitably reflected in limited detection capabilities (for higher concentration levels) and second, the reduced zinc readily forms various intermetallic compounds, especially with Cu^{II}, that may seriously interfere in its determination.

The possible detection of zinc(II) at the bare GCE and CPE was investigated next, confirming fully the above-mentioned less effective deposition and limited detection capabilities as one can see on the resultant voltammograms in **Fig. 15** and **Fig. 16**. Interestingly, the signal at the GCE had been split into two small signals of unknown nature. Because the overall response was again worse compared to that obtained with the CPE, the carbon paste-based substrate was selected for further studies.

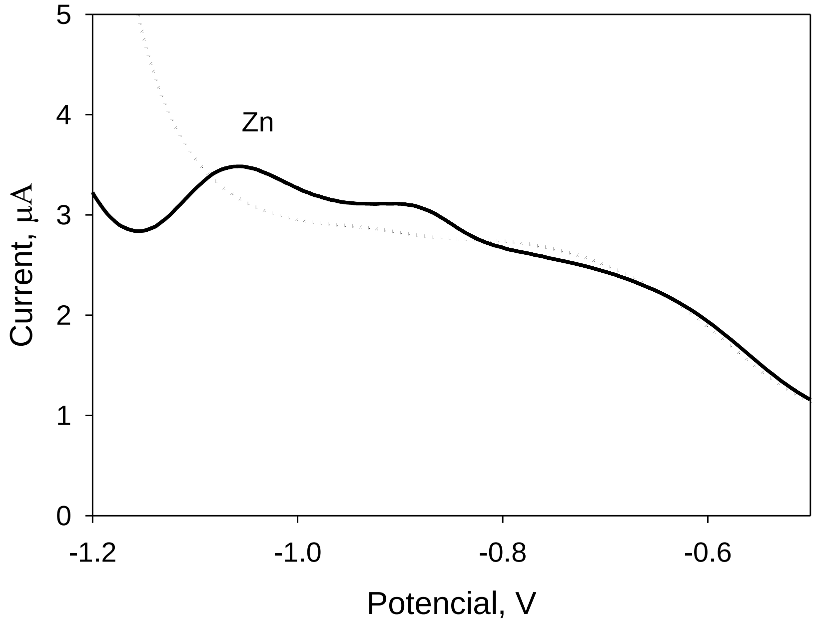

Figure 15. Square-wave voltammograms of Zn(II) at the glassy carbon substrate. Blank (dotted line), 60 µg L^{-1} (solid line). Deposition time was 120 s, deposition potential -1.45 V. Supporting electrolyte 0.1 mol L^{-1} acetate buffer (pH 4.5).

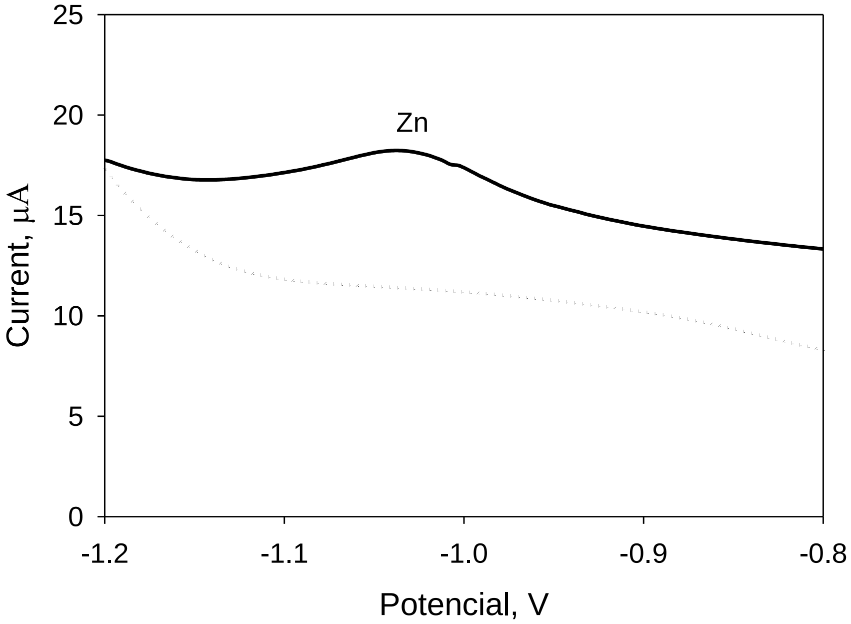

Figure 16. Square-wave voltammograms of Zn(II) at the carbon paste substrate. Blank (dotted line), 60 µg L^{-1} (solid line). Deposition time was 120 s, deposition potential -1.45 V. Supporting electrolyte 0.1 mol L^{-1} acetate buffer (pH 4.5).

3.6.3. Square wave anodic stripping voltammetry of zinc(II) at the GaF-CPE in acetate buffer

The respective test was made with GaFE operated in situ, when the concentrations of both Ga(III) and Zn(II) were similar to those in two previous experiments. All the measurements had been made in in 0.1 M acetate buffer under the same conditions and with already set parameters.

The result is depicted in **Fig. 17**, revealing that even rather narrow potential range of the GaF-CPE would enable to indicate the response of zinc, appearing as a sharp signal (with E_P of about −1.05 V vs. ref.) at the left foot of dissolution peak of gallium. Whereas the figure shows the particular experiment with one model concentration, the subsequent calibrations have resulted in finding that zinc could be detected within a concentration interval of *ca.* 10-50 µgL^{-1} Zn(II). Whereas the concentrations lower than 10 µg L^{-1} Zn(II) could not be detected due to the insufficient sensitivity (see commentary above), the concentrations above 50 µg L^{-1} Zn(II) were unachievable as well, due to the close position of both Zn- and Ga- reoxidation signals and their undesirable overlaps.

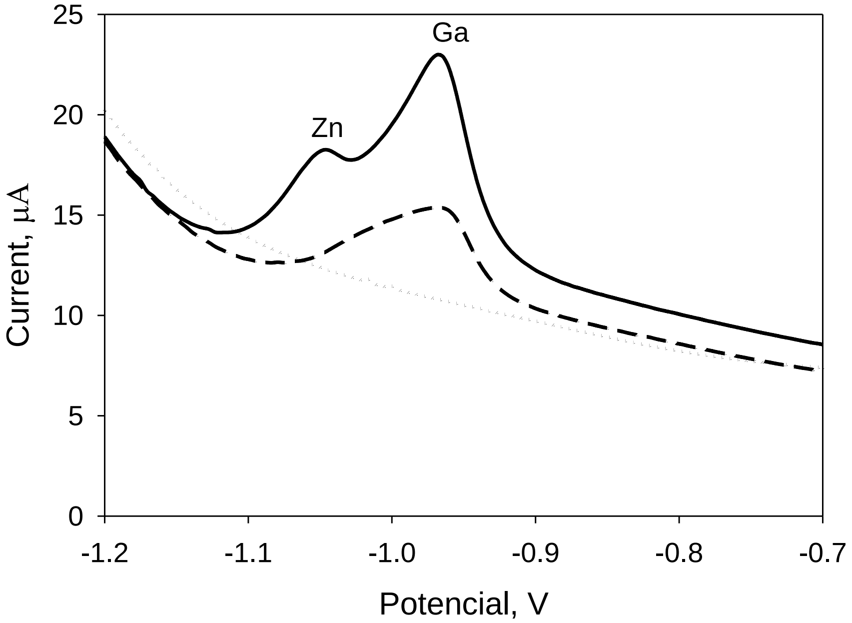

Figure 17. Square-wave voltammograms of Zn(II) at gallium film plated carbon paste electrode (GaF-CPE). Blank (dotted line), 5 mg L^{-1} Ga(III) (dashed line), 5 mg L^{-1} and 50 µg L^{-1} Zn(II) (solid line). Deposition time was 60 s, deposition potential -1.7 V. Supporting electrolyte 0.1 mol L^{-1} acetate buffer (pH 4.5).

3.6.4. Square wave anodic stripping voltammetry of zinc(II) at the GaF-CPE in other supporting media

A series of different supporting electrolytes was tested; namely: ammonia buffer (with pH 9), phosphate buffer (pH 7.5), 0.01 M HCl, 0.01 M $HClO_4$ (both pH ca. 2), and 0.1 M NaOH (pH ca. 13); some of these solutions with additions of 0.01 KCl, KBr, and citrate or even 0.001 M EDTA.

In fact, compared to 0.1 M acetate buffer and its use as model medium (described above), none of newly tested solutions led to any significant improvement of both peaks of interest and their mutual resolution. Perhaps, except diluted hydrochloric acid for which the respective voltammograms are shown in **Fig. 18**.

The set depicted documents a fine and smooth blank and, in two subsequent scans, a fairly proportional increase of the signal for zinc (with $E_P = -1.0$ V vs. ref.), whereas the magnitude of the (large) dissolution peak of gallium has remained practically unchanged. Only, one can notice its certain shift to the less negative potentials, which is a phenomenon typical for metal film electrodes and higher concentrations of the reoxidised species.

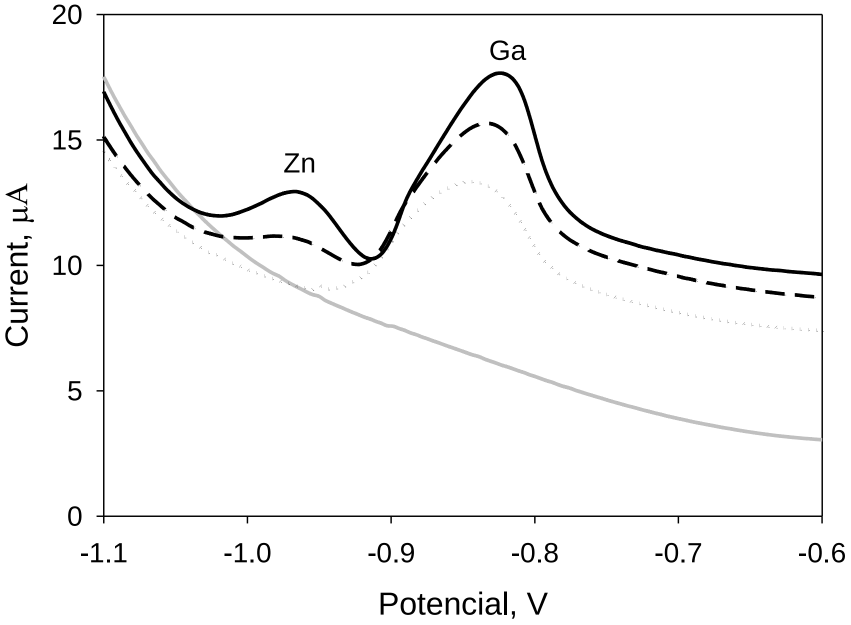

Figure 18. Square-wave voltammograms of Zn(II) at gallium film plated carbon paste electrode (GaF-CPE). Blank (grey line), 5 mg L^{-1} Ga(III) (dotted line), 5 mg L^{-1} and 50 µg L^{-1} Zn(II) (dashed line), 5 mg L^{-1} and 50 µg L^{-1} Zn(II) (solid line). Deposition time was 60 s, deposition potential -1.7 V. Supporting electrolyte 0.01 mol L^{-1} HCl solution.

CONCLUSIONS

1. When depositing Bi films on glassy carbon electrode it was found, that the addition of Br^{-1} changes the BiFE morphology making it more uniform and forming crystalline aggregates. The reoxidation peak of Bi was shifted to more negative potentials showing the electrocatalytic effect of bromide for the bismuth film.

2. The addition of the other metal ions to the deposition solutions caused changes in the morphology of the Bi film. Moreover, the morphology of Bi film with Cd was different from that with Pb. CVs at these films had rather low peaks of Cd or Pb and lower peak of Bi than that without additional metals. However, the SWASV this effect was observed only for the Bi-Cd film but in the case of Bi-Pb film the Pb peak was much higher than the Bi one, as well as Bi peak was similar to that without any additional metal. Cd was slowing the Bi film deposition and Pb was catalyzing this deposition.

3. Nanoparticle-structured film was obtained when Bi film was deposited together with both Cd and Pb. Although, the CVs showed even lower reoxidation peaks of all metals than at Bi-Cd or Bi-Pb films but SWASVs had bigger peak of Cd, the same peak was of Pb, and Bi was similar to the peak without any metals. Pb is catalyzing deposition of other metals on the electrode surface.

4. Zn(II), Cd(II), Cu(II) and Pb(II) ions were determined in the water samples using bismuth film electrode. The linear calibration curve of each metal was obtained from SWASV measurements with increasing concentrations of Zn(II), Cd(II), Cu(II) and Pb(II) in the acetate buffer (pH 4.5). Good linear responses of the peak area vs. concentration were obtained for Zn(II), Cd(II), Pb(II) and Cu (II) up to the concentration level of 150, 130, 90 and 100 $\mu g\ L^{-1}$ and correlation coefficients of 0.997, 0.997, 0.999 and 0.998 respectively.

5. The possibilities of gallium film plating were studied. The glassy carbon substrate was chosen for optimization. The optimized deposition conditions were: supporting electrolyte 0.1 M acetate buffer, deposition potential -1.7 V, deposition time 120 s, deposition temperature 40°C.

6. The gallium influence on Pb(II) and Cd(II) deposition at the glassy carbon electrode was studied. The Ga(III), Cd(II) and Pb(II) were deposited *in situ* and *ex situ*. It has been shown that Pb(II) and Cd(II) peaks increased significantly in the presence of gallium when deposited *in situ*. It could be explain due to gallium possibility to form intermetallic compounds with other metals.

7. The possibilities to determine Zn(II) on gallium film electrode using different carbon substrates were studied. It has been shown that gallium film plated *in situ* and preferably onto the carbon paste-based support can be employed as a detection tool in anodic stripping voltammetry of zinc(II) at the trace concentration level (in an interval of 10-50 µM Zn(II)).

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1. G. Grincienė, A. Selskienė, **R. Verbickas**, E. Norkus, R. Pauliukaitė, *Peculiarities of electrochemical Bi film formation in the presence of bromide and heavy metal ions*. Electroanalysis **21**(15) (2009) 1743-1749.
2. O. Gyliene, G. Grincienė, **R. Verbickas**, R. Butkienė, A. Misiunas, I. Viteniene, *Heavy metal removal from solutions using metallic iron*. Transactions of the Institute of Metal Finishing **91**(4) (2013) 214-220.

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1. R. Pauliukaitė, G. Grincienė, R. Verbickas, *Application of bismuth film electrode for electrochemical determination of some heavy metals,* 1st International Conference „METEAU – Metals and related substances in drinking waters“, Antalya, Turkey, 2007, p. 105.
2. E. Norkus, I. Stalnionienė, D.C. Crans, G. Grincienė, K. Prūšinskas, R. Verbickas, *Interaction of piridine- and 4-Hydroxypyridine-2,6-dicarboxylicacids with heavy metals ions in aqueous solutions*, 2nd International Conference „METEAU – Metals and related substances in drinking waters“, Lisbon, Portugal, 2008, p. 44.
3. R. Verbickas, G. Grincienė, A. Selskienė, R. Pauliukaitė, E. Norkus**,** *Peculiarities of electrochemical Bi film formation in the presence of bromide and heavy metal ions*, 9th National Lithuanian Conference „Chemija 2009“, Vilnius, 2009, p. 50.
4. R. Verbickas, E. Norkus, I. Švancara, *Possibilities and Limitations of the Determination of Zinc(II) at Gallium Film Electrodes,* Doctoral internships in science centers of foreign countries conference, Vilnius, 2013.

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Sunkiųjų metalų inversinio elektroanalizinio nustatymo tyrimai

Santrauka

Šiame darbe tiriama galio ir bismuto plėvelinių elektrodų formavimo *in situ* ir *ex situ* metodais ypatumai skirtingose sistemose. Optimizuotos bismuto ir galio plėvelinių elektrodų panaudojimo sąlygos sunkiųjų metalų koncentracijos nustatymui.

Atliekant bismuto plėvelės nusodinimą ant stikliškosios anglies elektrodo nustatyta, kad papildomas Br^- pridėjimas į tiriamąjį tirpalą keičia bismuto plėvelės morfologines savybes ir formuojasi tolygesnė bismuto plėvelė sudarydama kristalines struktūras. Reoksidacinė bismuto smailė pasislenka į neigiamesnių potencialo verčių pusę, kas rodo elektrokatalizinį Br^- efektą bismuto plėvelės formavimuisi. Nustatyta, kad Cd(II) pridėjimas į tiriamąjį tirpalą lemia lėtesnį bismuto plėvelės nusodinimą, o Pb(II) pridėjimas katalizuoja bismuto plėvelės nusodinimą. Taip pat nustatyta, kad Pb(II) katalizuoja ir kitų metalų jonų nusodinimą. Bismuto plėvelinis elektrodas sėkmingai pritaikytas sunkiųjų metalų Cu(II), Zn(II), Pb(II), Cd(II) koncentracijos nustatymui pramoniniuose vandens mėginiuose. Gautos Zn(II), Cd(II), Cu(II) ir Pb(II) kalibravimo kreivės, kurių korealiacijos koeficientai atitinkamai yra 0,997, 0,997, 0,999 ir 0,998.

Optimizuotos galio plėvelės nusodinimo sąlygos ant stikliškosios anglies elektrodo. Geriausi rezultatai gauti atliekant galio plėvelės nusodinimą 0,1 M acetatiniame buferyje (pH = 4,5) 40^o C temperatūroje. Optimizuotas nusodinimo laikas ir potencialas atitinkamai yra 120 s ir -1,7 V. Tiriant galio jonų įtaką Pb(II) ir Cd(II) nusodinimui pastebėta, kad Pb(II) ir Cd(II) analiziniai signalai žymiai padidėja atliekant metalų jonų nusodinimą ant stikliškosios anglies elektrodo *in situ* būdu papildomai esant 1 mg L^{-1} Ga(III) koncentracijai tiriamajame tirpale. Optimalus nusodinimo laikas 120 s, o nusodinimo potencialas -1,5 V. Nustatyta, kad galio plėvelės nusodintos *in situ* būdu ant anglies pastos elektrodo gali būti naudojamos anodinėje inversinėje voltamperometrijoje Zn(II) koncentracijos nustatymui 10-50 μgL^{-1} ribose.

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