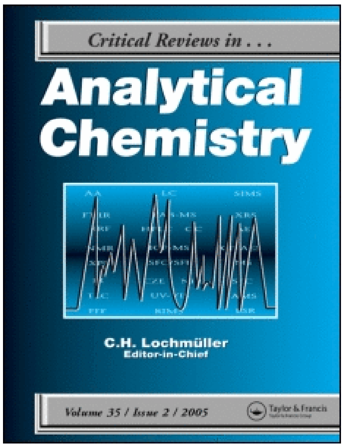

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Analytical Application of Silver Composite Electrode

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ABSTRACT: Silver composite electrode prepared from silver and graphite powder and methacrylate resin presents a suitable sensor for the voltammetric measurements. Cathodic polarization of this electrode enables the determination of nitrates, nitrites, organic nitro compounds, and halide ions. The use of this electrode in differential pulse anodic stripping voltammetry enables the direct determination of lead in natural water samples without the elimination of the presence of surface-active substances or the dissolved oxygen. The effect of under potential deposition at the composite electrode differs from that effect produced by metallic silver electrode mainly at low concentrations of the deposited metal.

KEY WORDS: silver composite electrode, voltammetry, nitrates, nitrites, halogenides, lead.

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I. INTRODUCTION

The possible analytical applications of a silver composite electrode prepared by dispersing of powder silver in methacrylate resin are presented in this article. A composite electrode is defined as a material consisting of at least one conductor phase and at least one insulator phase.[1] The surfaces of these electrodes consist of either ordered arrangement or random arrangement of conductor regions separated from one another by an insulator. Composite electrodes offer potential advantages compared with metallic or glassy carbon electrodes (electrodes consisting of a single conducting phase), for example, lower cost, less weight, higher signal-to-noise ratio, the possibility of chemical modification of the conductor or insulator phase.

The application of metallic silver electrodes in anodic stripping voltammetry is not so common,[2,3] and higher interest was devoted to the cathodic polarization of these electrodes.[4,5,6] The results obtained by cyclic voltammetry and by anodic stripping voltammetry have shown the differences between the voltammetric behavior of metallic and composite silver electrodes. The effect of underpotential deposition (UPD), which is a typical effect of metallic electrodes,[7,8,9] was also pronounced in the case of the composite silver electrode. The composite silver electrode was also applied for the determination of nitrates, nitrites, and halides, where the cathodic polarization is used.

II. BACKGROUND SECTION

A. Apparatus

A computer-controlled voltammetric analyzer ECO-TRIBO Polarograph (POLAROSENSORS, Ltd., Prague, Czech Republic), equipped by POLAR.PRO for Windows v. 4.0 software,[10] was used for the measurements. A 1.0 *M* Ag/AgCl (KCl) electrode was used as reference and platinum wire as counter electrode. If necessary, nitrogen (99.99%) was used for the removal of oxygen from the measured solutions.

The cell and the glass implements were cleaned with chromsulfuric acid and washed thoroughly with bidistilled water. All measurements were realized at room temperature.

B. Reagents

The mentioned chemicals were of analytical purity grade “p. a.” (Lachema, Brno, Czech Republic). Bidistilled water was used for preparation of all solutions.

For the composite electrode preparation silver powder (J. Matthey, Inc., USA), particle size 5 to 10 μm was used. An insulating component of the composite electrode was the methacrylate resin (Spofa, Praha, Czech Republic). Graphite powder used was Graphite, extra pure (Merck, Ltd., Praha, Czech Rep.), particle size below 50 μm.

C. Construction of the Composite Electrode

The silver composite electrode was prepared by mixing the methacrylate resin with an appropriate amount of silver and graphite powder. The resulting mixture was homogenized by mixing. The polymerization liquid was then added and mixed until a plastic paste was formed. The resulting paste was let to sit for 5 min and after that the paste was pressed into the tip of the electrode body — Perspex tube 90 mm long, 12 mm outer diameter, 2 mm inner diameter), and thus a 2-mm-diameter composite disc electrode was formed. After 6 h of the time of polymerization at 60°C, the electrical contact of the electrode was realized by filling the inner part of the electrode body with graphite powder, into which the copper wire was inserted. The electrode surface was brushed with emery paper of various granulity and at the end polished gently with alumina paste (0.03 μm).

D. Mathematical Description of the Underpotential Deposition Effect

If a metallic electrode is applied for the cyclic voltammetric measurement of a metal ion, two cathodic, and two anodic peaks are usually obtained. This phenomenon is explained by the underpotential deposition effect that describes the formation (deposition) of a metal monolayer at potential more positive than the reversible Nernst potential. This means that the monolayer deposition occurs before the bulk deposition starts. In the anodic polarization, on the other hand, the dissolution of the bulk takes place before the monolayer dissolution.

The peak corresponding to the monolayer adsorption/dissolution is fully described by two parameters: the potential shift (ΔE_p) and the half-peak width ($\delta_{1/2}$). The potential shift ΔE_p is defined as the difference between the peak potentials of adsorption/dissolution peaks corresponding to the monolayer and to the bulk ($\Delta E_p = E_r - {}_{ML}E_r(\theta)$ – where E_r means the Nernst potential and ${}_{ML}E_r(\theta)$ potential of the monolayer peak). In the first approach[7,11] it is possible to calculate the position of the monolayer peak applying the classic Nernst law:

$$E_r = E_0 + \frac{RT}{zF} \ln \frac{a_{ox}}{a_{red}} \qquad (1)$$

where a_{Ox} / a_{red} means activity of oxid./red. compound, and E_r means the Nernst potential. One can suppose that for the activity of a metal monolayer a_{ML} is valid: $a_{ML} = f_{Me}.\theta$ for $0 \leq \theta \leq 1$ and $a_{ML} = f_{Me} = 1$ for $\theta > 1$, where θ is the surface coverage and f_{Me} activity coefficient. After insertion of these expressions into the Eq. 1 one obtains

$${}_{ML}E_r(\theta) = E_0 + \frac{RT}{zF} \ln \frac{c_{Me^{z+}} f_{Me^{z+}}}{\theta \ f_{Me}} > E_r \qquad (2)$$

where $f_{Me}{}^{z+}$- activity coefficient of metal ion in the solution, f_{Me}- activity coefficient of metal ion in the bulk, $c_{Me}{}^{z+}$ concentration of metal ion.

There are some other possibilities of mathematic description of this effect (7), but practically all of them are purely formalistic and do not involve all the parameters: influencing metal ions concentration, nature of the electrolyte, specific interaction occurring between the electrolyte and the solid phase.

III. PRACTICAL APPLICATIONS

A. Composition of Composite Silver Electrode and its Preparation for Measurement

The described mode of the preparation of the used composite electrodes leads to the preparation of an electrode the surface of which consists of a random arrangement of silver particles (particle size below 10 μm) separated from one another by graphite and methacrylate resin particles.

For the initial measurements two types of silver composite electrode were prepared, the first containing 10% of silver and 90% of methacrylate resin and the second 20% of silver and 80% of the resin. The electrodes were tested by cyclic voltammetric measurement in perchloric acid solutions. The composite electrode with 10% of silver showed lower conductivity and not very good reproducibility of the measurement. The electrode with 20% of silver had a very good conductivity and the measurements were well reproducible. Further experiments showed that the addition of graphite powder into the electrode material enables easier mechanical activation of the electrode surface and prolonged the electrode stability and the reproducibility of the results. For further measurements therefore electrodes were prepared consisting of 20% silver, 20% graphite, and 60% methacrylate resin.

Freshly prepared electrodes with mechanically polished surface were first activated by cyclic voltammetry, 25 cycles with the scan rate 250 $mV.s^{-1}$, using the same supporting electrolyte, which should be used for the further voltammetric measurement.

To improve the repeatability of the measurement, the potential of the electrode was kept at a defined value for a defined time interval before each measurement. The corresponding potential values and time intervals depend on the quality of the measured analyte and were determined empirically.

B. Cathodic Polarization of Silver Composite Electrode

1. Voltammetry of Nitrate Ions

After the mechanical treatment (polishing of the electrode surface), the composite electrode was activated by cyclic voltammetry (25 cycles from –0.10 to –1.50 V, scan rate 250 $mV.s^{-1}$, supporting electrolyte 0.1 *M* NaOH).

Using differential pulse voltammetry (DPV) the reduction peak of nitrate ions appeared at the potential –0.80 V and the reduction peak of nitrite ions at the potential –1.25 V. To improve the repeatability of the measurement, the potential of the electrode before each measurement was kept for 0.2 s at the potential of 0.10 V and then for the same time interval at the potential of -1.50 V. This potential jump was repeated ten times and immediately after that the potential scan from –0.10 to –1.40 V was started. The height of this peak at the potential –0.80 V depended linearly on the nitrate ion concentration in the range from 5 to 400 $mg.L^{-1}$. Linear least squares parameters were determined as: correlation coefficient 0.9995, slope 143.7 nA per 1 $mg.L^{-1}$, limit of detection 4.5 $mg.L^{-1}$.

While the silver disc electrodes exhibit peak-shaped responses when linear scan voltammetry (DC) was applied, the response of DC voltammetric measurement of nitrate ions in sodium hydroxide media with composite silver electrode had a sigmoidal form. In this case the limiting current increased nonlinearly (parabolic) with increasing scan rate. This dependence measured with silver metal electrode is, on the other hand, linear. Nonlinear course of these dependences has been found in the study of microelectrode ensembles.[12] The obtained results led to the conclusion that the composite electrode with random distribution of silver particles on the electrode surface exhibits the electrochemical behavior similar to the ensemble of microelectrodes.[1,12–14]

From an analytical point of view, the application of the composite silver electrode is advantageous. The preparation of the electrode is simple and economically acceptable. The activation of the electrode surface by time and potential defined polarization before each measurement assures good reproducibility of the obtained results. Using this electrode the content of nitrate ions was determined in the samples of river and tap water; the obtained results were in good agreement with the results obtained by a spectrophotometric method.[13]

With composite silver electrode the organic nitrocompounds (nitrophenols, etc.) can be reduced similarly as nitrate ions.

2. Voltammetry of Halide Ions

Silver electrode was applied for the determination of halide ions using the cathodic stripping voltammetry.[15] The same principle can be applied for the cathodic stripping voltammetry of halide ions using the silver composite electrode.

Because halide ions were measured in nitric acid solution, the activation of the electrode surface was realized by cyclic voltammetry (25 cycles from –0.10 to –0.70 V, scan rate 150 mV.s^{-1}) in 0.1-M HNO_3. To improve the repeatability of the results, the electrode was kept at the potential –0.50 V for the time of 1 s before each measurement.

The determination of halide ions with silver composite electrode was carried out by DC cathodic stripping voltammetry using 0.1 M HNO_3 as a base electrolyte. The parameters of the measurement were deposition potential 0.30 V, initial potential 0.30 V, final potential –0.50 V, scan rate 150 mV.s^{-1}. The cathodic peak of chloride ions appeared at the potential 0.08 V. At the deposition time 60 s, a linear dependence of the measured cathodic current vs. chloride ions concentration was obtained in the concentration interval from 300 to 1500 ppb of chloride ions. The slope of this dependence was 7.80 nA per 1 μA.L^{-1}, correlation coefficient 0.999.

Chloride ions can be determined in the presence of iodides. Under the given conditions iodide ions yield a sigmoidal response (double wave) in the potential range from –0.20 to 0.40 V and do not interfere the chloride ions determination. In Figure 1 the peak of chloride ions measured in the presence of an excess of iodide ions is presented.

The voltammetric behavior of bromide ions is more complicated. The bromide response obtained by cathodic DC stripping voltammetry is a wide peak at the potential –0.14 V, this potential is shifted to more negative values with increasing bromide ions concentration or with prolonged deposition time see (Figure 2). These effects make impossible the determination of chlorides in the presence of a higher excess (five times) of bromide ions.

C. Anodic Polarization of Composite Silver Electrode

1. Cyclic Voltammetry

As mentioned above, the application of silver electrode in anodic stripping voltammetry

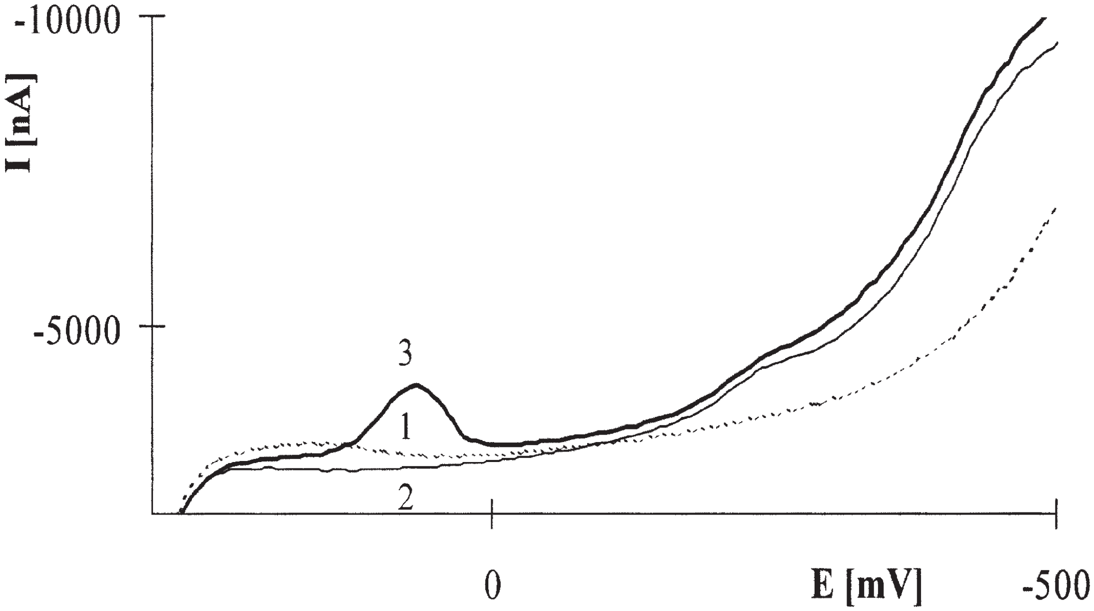

FIGURE 1. Cathodic stripping DC voltammetry of chloride ions in the presence of iodide ions. Silver composite electrode, deposition potential 0.30 V, deposition time 30 s, scan rate 150 mV.s^{-1}, 20 cleaning scans from -0.45 to 0.30 V with scan rate 500 mV.s^{-1} before each measurement. Curve (1): 0.1 M HNO_3, (2): 5.5 mg.L^{-1} I^- in 0.1 M HNO_3, (3): 10 mg.L^{-1} Cl^- and 5.5 mg.L^{-1} I^- in 0.1 M HNO_3.

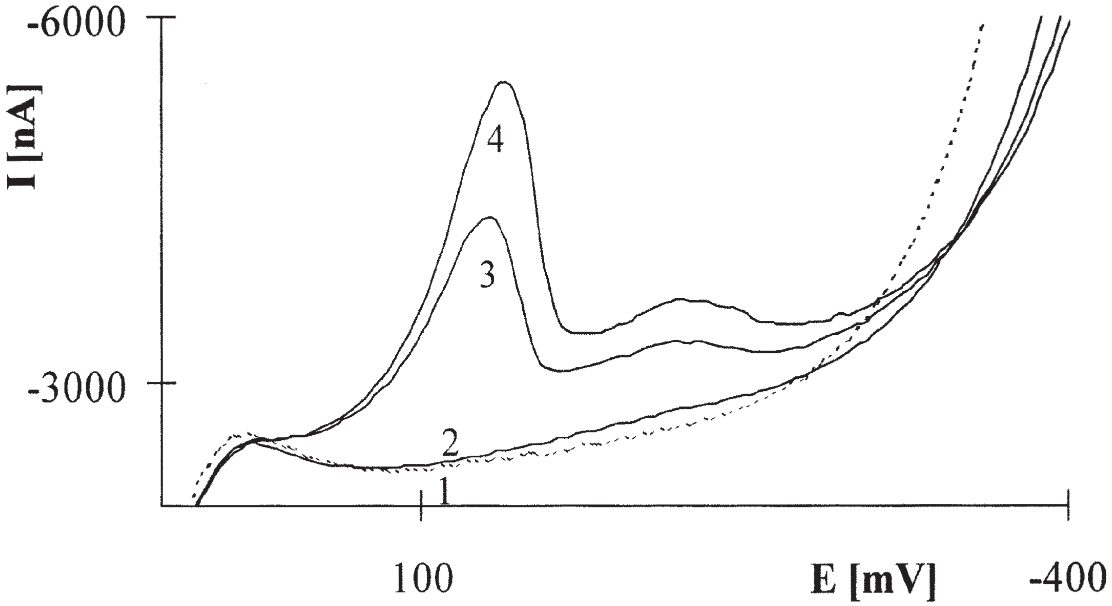

FIGURE 2. Cathodic stripping DC voltammetry of chloride ions in the presence of bromide ions; Silver composite electrode, deposition potential 0.30 V, deposition time 60 s, scan rate 150 mV.s^{-1}, 20 cleaning scans from –0.45 to 0.30 V with scan rate 500 mV.s^{-1} before each measurement. Curve (1): 0.1 mol.L^{-1} HNO_3, (2): 1.1 mg.L^{-1} Br^- in 0.1 *M* HNO_3, (3) 0.8 mg.L^{-1} Cl^- and 1.1 mg.L^{-1} Br^- in 0.1 *M* HNO_3, (4) 1.0 mg.L^{-1} Cl^- and 1.1 mg.L^{-1} Br^- in 0.1 *M* HNO_3.

was devoted primarily to the determination of lead.[2,3] The possibility of the application of composite silver electrode in ASV therefore was examined first by cyclic voltammetry of lead(II) ions. The effect of UPD well known from the measurements with silver electrode also appeared at the measurement with silver composite electrode. Cyclic voltammogram of 2.10^{-4} mol.L^{-1} lead in 0.1 *M* $HClO_4$ yields a cathodic sigmoidal response at the potential –0.35 V (the more negative cathodic signal is covered by the current due to hydrogen evolution) and two anodic peaks at the potential values –0.44 and –0.35 V (see Figure 3). The anodic peak at the more positive potential can be attributed to the monolayer dissolution. In neutral medium (0.05 *M* KNO_3) the anodic part of the cyclic voltammogram corresponds to the anodic part obtained in acidic medium (monolayer and bulk dissolution peaks). In the cathodic part, the reduction signal of lead(II) ions is overlapped by a sigmoidal response (high wave) at the potential -0.55 V. This phenomenon was not examined in detail, the fact that the height of this wave increases with increasing concentration of added acid ($HClO_4$ or HNO_3) led, however, to the conclusion that this signal corresponds to the catalytic reduction of hydrogen ions.

The effect of chloride ions on anodic stripping of lead in acidic solutions was found quite expressive. In the presence of chloride ions the underpotential shift ΔE_p (see Background Section paragraph D) decreased from the value 180 mV to 100 mV and the area under the anodic monolayer peak was enlarged two times (see Figure 3). These findings led to the conclusion that similarly as in the case of metallic silver electrode, the chloride ions interact with the substrate of the electrode and that the lead atom adsorption is accompanied by chloride ions desorption, where both processes contribute to the current in the same direction and thus produce a larger apparent surface charge.[16] Similar behavior was observed in 0.1 and 0.5-*M* KCl base electrolyte, where the shape of the monolayer and bulk deposition response is very well developed (see Figure 4).

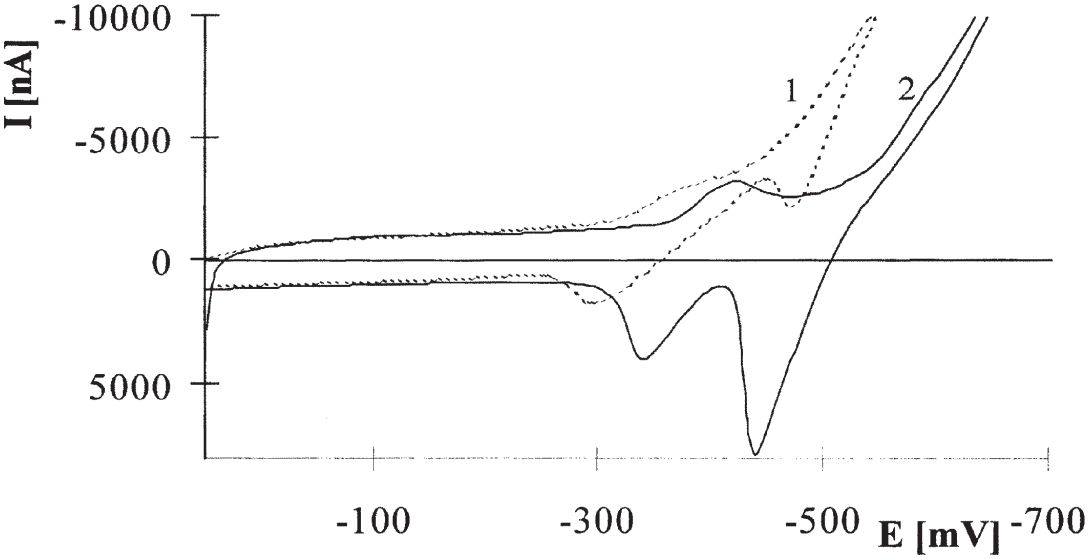

FIGURE 3. Cyclic voltammogram of lead(II) in perchloric acid and with added potassium chloride. Silver composite electrode, base electrolyte 0.1 *M* $HClO_4$, scan rate 25 $mV.s^{-1}$, 25 $mg.L^{-1}$ lead(II), concentration of KCl (in $mol.L^{-1}$): curve (1) 0, curve (2) 0.05.

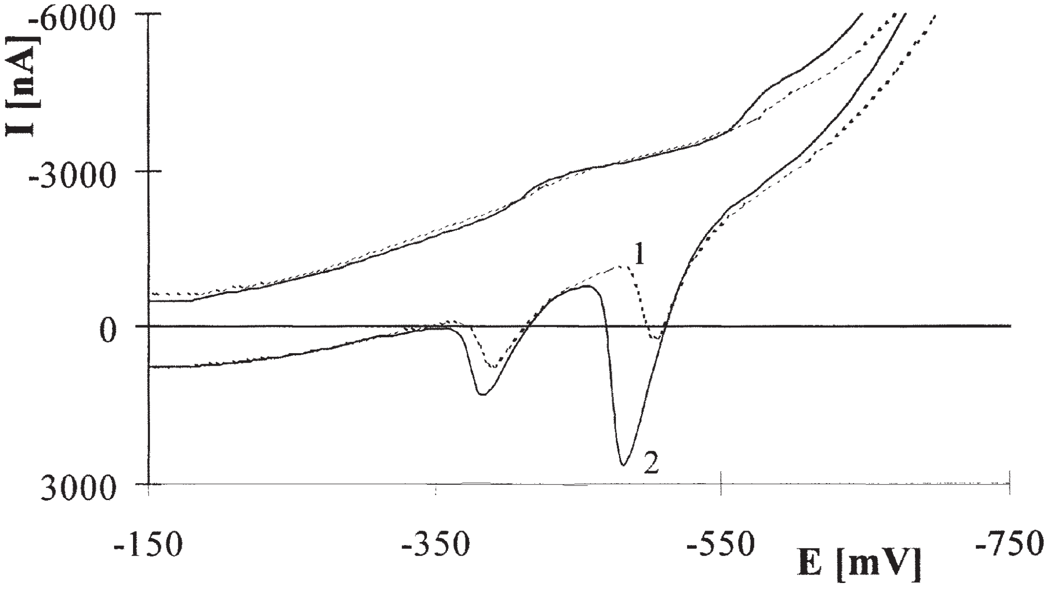

FIGURE 4. Cyclic voltammogram of lead(II) ions in potassium chloride electrolyte. Silver composite electrode, scan rate 5 $mV.s^{-1}$. Curve (1): 0.5 $mol.L^{-1}$ KCl and 1.10^{-4} $mol.L^{-1}$ Pb^{2+}, (2) 0.5 $mol.L^{-1}$ KCl and 2.10^{-4} $mol.L^{-1}$ Pb^{2+}.

An interesting phenomenon presents the cyclic voltammogram of lead (II) ions recorded in 0.1 *M* $HClO_4$ a 0.05 *M* KCl medium with varied polarization rate (see Figure 5). The height of the anodic peak corresponding to the monolayer dissolution increases linearly with increasing scan rate in the interval from 20 to 200 $mV.s^{-1}$, while the height of the more negatively situated peak — bulk dissolution — decreases by approx. 10% in the same scan rate interval.

The comparison of the shape of the cyclic voltammograms of lead ions obtained with metallic silver electrode and composite silver electrode showed that the voltammetric behavior of the composite electrode remains basically the behavior of a single-crystal silver electrode. It has been observed that on Ag(111) electrode the deposition as well as stripping of a monolayer occurs within an extremely narrow potential range, while at polycrystalline surface a broader potential range was obtained. Cyclic voltammogram (2.10^{-4} $mol.L^{-1}$ Pb^{2+} in 0.5 *M* $NaClO_4$, scan rate 1 $mV.s^{-1}$) measured with the composite silver electrode showed a sigmoidal curve during the cathodic polarization and a sharp anodic peak with the half-peak width of 23 mV. The difference between the potential values of the anodic peak and "half-wave" potential of the cathodic response corresponds to 18 mV. Under identical conditions the half-peak width obtained with Ag(111) electrode has the value 18 mV and the difference between the potential of anodic and cathodic peaks was 28 mV. The half-peak width obtained with polycrystalline silver electrode had the value 45 mV and the difference of the anodic and cathodic peaks potentials had the value 48 mV. The published results let to the conclusion that on a single crystal surface (Ag(111)) the deposition represents a first-order phase transition (interaction parameter from Langmuir (Frumkin) isoterm $g = -4$)[16] and not an adsorption with strong attraction among the adatoms, which should be preferred at polycrystalline Ag electrode.[7] The presented data confirm that the voltammetric behavior of the silver composite electrode is nearer to

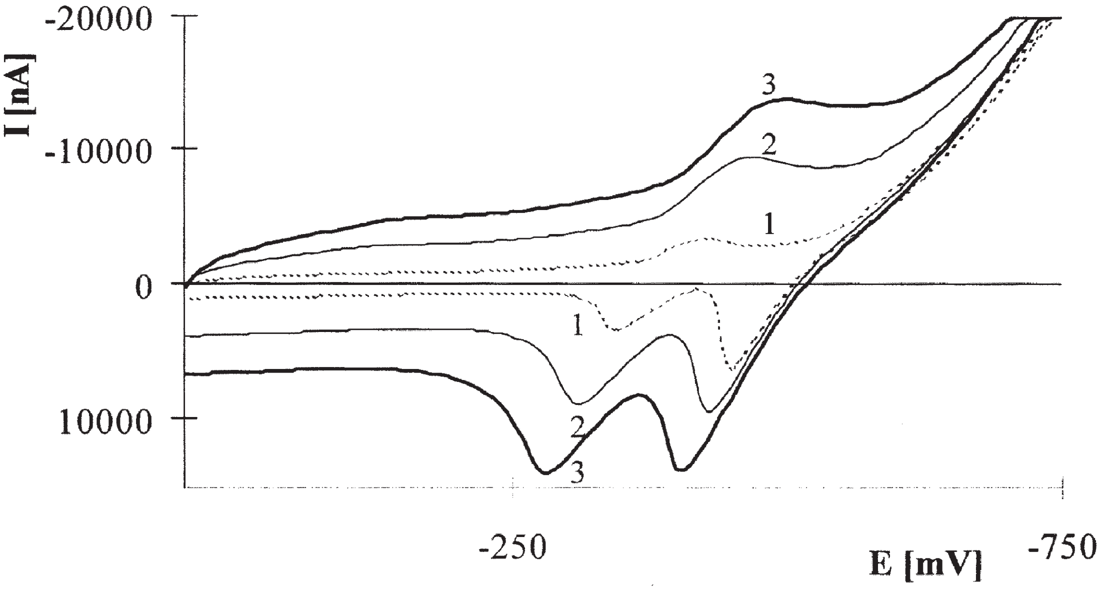

FIGURE 5. Cyclic voltammogram of lead(II) ions in potassium chloride electrolyte with varying scan rates. Silver composite electrode, electrolyte 0.1 *M* $HClO_4$ and 0.05 *M* KCl and 2.10^{-4} *M* Pb^{2+}. Scan rate: curve (1) 25 $mV.s^{-1}$, curve (2) 125 $mV.s^{-1}$, curve (3) 250 $mV.s^{-1}$.

the behavior of a single crystal silver electrode.

2. Anodic Stripping Voltammetry with Composite Silver Electrode

The results obtained by cyclic voltammetry with silver composite electrode confirm the possibilities of the application of this electrode in anodic stripping voltammetry. In anodic stripping voltammetry of lead the differential pulse technique was applied (pulse amplitude 75 mV, pulse width 100 ms, interval between pulses 200 ms, scan rate 20 mV.s $^{-1}$, deposition potential –0.80 V and rest time 5 s). The resulted anodic polarization yielded well-developed anodic peaks. Similarly, as at the DPASV measurement with metallic silver electrode, the dissolved oxygen present in the measured solution does not influence the shape of the resulted polarization curves recorded with the composite silver electrode. To improve the repeatability of the results, the potential of the working electrode was kept at the potential 0.25 V for 3.5 s before each measurement.

In 0.1 *M* $HClO_4$ at low concentration of lead(II) ions (5 to 100 ppb, deposition time 200 s) one anodic peak at the potential –0.42 V was obtained by DPASV. The anodic current of this peak increased linearly with increasing lead(II) ions concentration (slope 3.50 nA/μg.L^{-1}). Under identical conditions two anodic peaks (–0.42 and –0.57 V) at higher lead (II) concentration (200 to 1000 ppb, 60 s deposition time) were obtained. Corresponding anodic currents increased linearly with increased lead(II) ions concentration, the slope of this dependence had a value 1.50 nA per 1 μg.L^{-1} for the more positive peak and 0.65 nA per 1 μg.L^{-1} for the more negative peak. The more positively situated peak corresponds evidently to the monolayer stripping, the more negative to the bulk stripping.

The effect of chloride ions on deposition and stripping of lead clearly manifested in cyclic voltammetry is advantageous from the analytical point of view in stripping voltammetry. It was observed that the height of the more positive anodic peak of lead in perchloric acid solution increased linearly with increased Cl^--ions concentration up to 3.10^{-3} *M* and nonlinearly at higher concentration, and simultaneously the peak potential is shifted to more positive potential values. The DPASV measurement carried out under identical condition as described above in 0.1 *M* $HClO_4$ and 0.01 *M* KCl medium showed that the dependence of lead ions concentration (5 to 100 ppb, 200 s deposition time) on the value of the anodic current of the peak at the potential –0.39 V was linear with the slope value 14.55 nA per 1 μg.L^{-1} (Figure 6). The more negative peak (bulk stripping) is not measurable and does not change with increasing lead(II) ions concentration. In the concentration range from 100 to 2500 ppb of lead (60 s deposition time), the dependence of the anodic current of the peak at the potential –0.39 V on lead(II) ions concentration was found linear with the slope 2125 nA per 1 μg.L^{-1}. Under these conditions the second stripping peak also appeared at the potential -0.54 V, the corresponding anodic current increased nonlinearly with increased lead (II) ions concentration and its maximum height reached 10% of the height of the monolayer stripping peak (Figure 7). As follows from the presented data, the DPASV curves obtained with composite silver electrode differ substantially from similar curves obtained with metallic silver electrode. Further, it has been found that the DPASV of lead is strongly affected also by the hydrogen and chloride ions concentration. A strange phenomenon was observed in DPASV of lead carried out in 0.25 *M* KCl solution. As shown on Figure 8, two anodic peaks of practically identical heights were obtained and the corresponding anodic current values increased linearly with increasing lead(II) ions concentration in the range

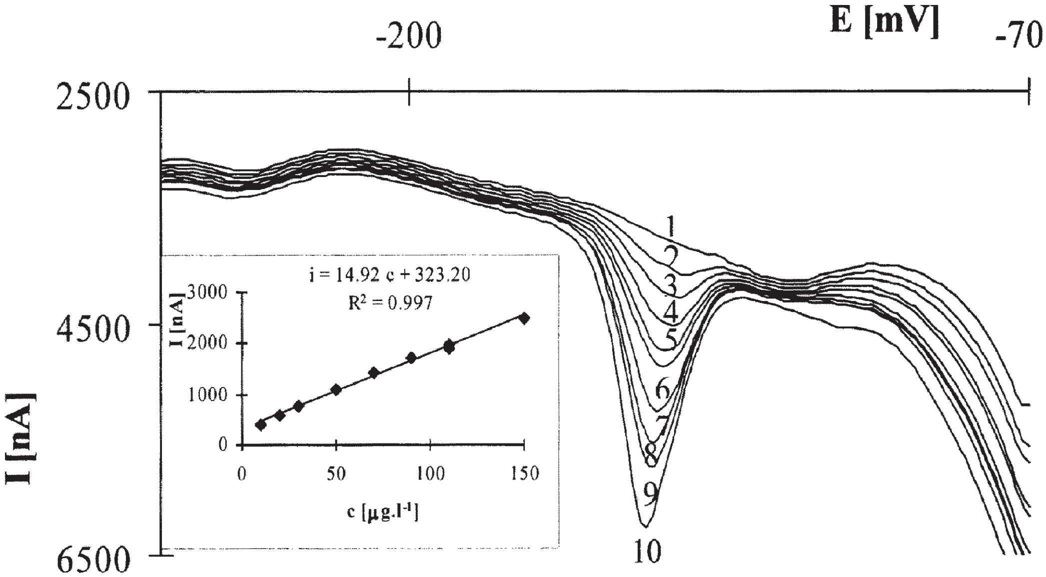

FIGURE 6. DPASV of lead(II) in perchloric acid and potassium chloride electrolyte. Silver composite electrode, base electrolyte 0.1 *M* $HClO_4$ and 0.01 *M* KCl, deposition potential –0.85 V, deposition time 200 s, rest time 5 s, scan rate 20 $mV.s^{-1}$, cleaning potential 250 mV and cleaning time 3.5 s, concentration of lead (in $\mu g.L^{-1}$): (1) 0, (2) 10, (3) 20, (4) 30, (5) 40, (6) 50, (7) 70, (8) 90. (9) 110, (10) 150.

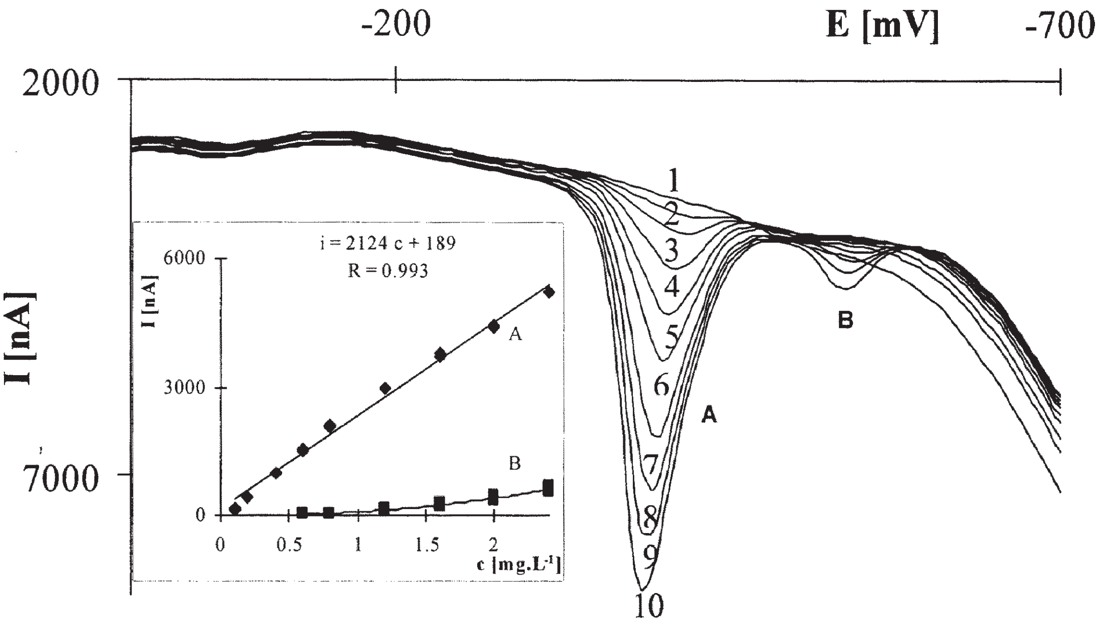

FIGURE 7. DPASV of lead(II) in perchloric acid and potassium chloride electrolyte. Silver composite electrode, base electrolyte 0.1 *M* $HClO_4$ and 0.01 *M* KCl, deposition potential –0.85 V, deposition time 60 s, rest time 5 s, scan rate 20 $mV.s^{-1}$, cleaning potential 250 mV and cleaning time 3.5 s, concentration of lead (in $mg.L^{-1}$): (1) 0, (2) 0.1, (3) 0.2, (4) 0.4, (5) 0.6, (6) 0.8, (7) 1.2, (8) 1.6, (9) 2.0, (10) 2.4.

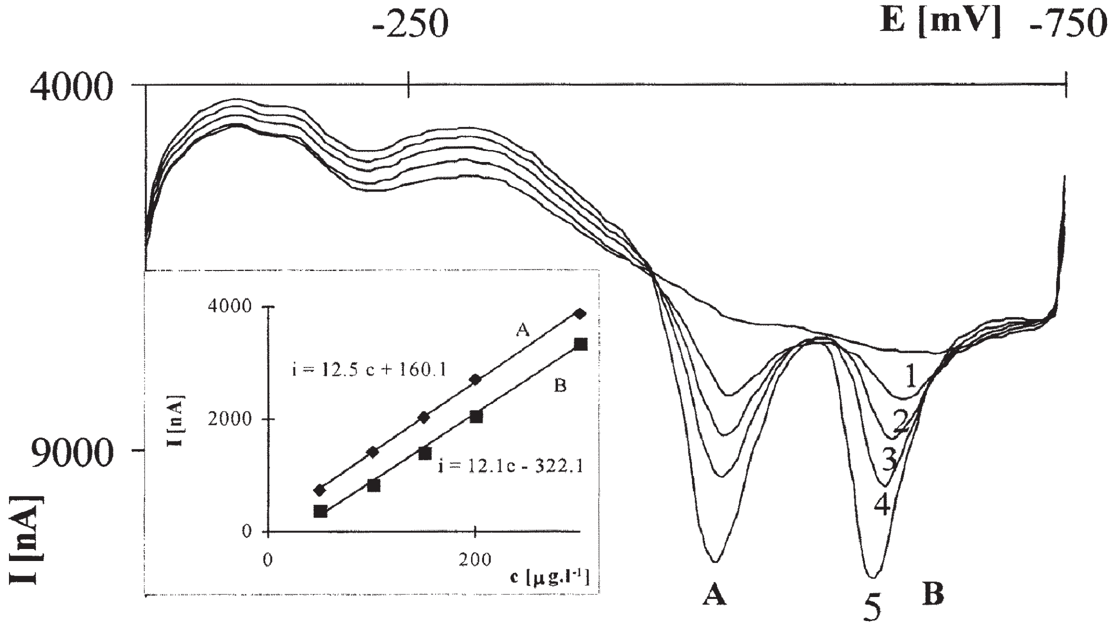

FIGURE 8. DPASV of lead(II) in potassium chloride electrolyte. Silver composite electrode, base electrolyte 0.25 *M* KCl, deposition potential –0.85 V, deposition time 90 s, rest time 5 s, cleaning potential 250 mV and cleaning time 3.5 s, concentration of lead (in μg.L^{-1}): (1) 0, (2) 50, (3) 150, (4) 200, (5) 300.

from 50 to 300 ppb. This phenomenon takes place only in neutral solutions with lower lead (II) ions concentration. As already shown, the cyclic voltammogram carried out in 0.1, 0.25, and in 0.5 *M* KCl solutions with higher lead(II) ions concentration (25 mg.L^{-1}) has the shape of monolayer and bulk deposition and stripping similarly as it has been obtained in acidic media and potassium chloride (see Figure 4).[1,3,7] The difference in the course of DPASV curves obtained with metallic and composite silver electrodes results most probably from the different surface structure of both types of electrodes. From an analytical point of view, the application of composite silver electrode in acidic solutions containing chloride ions is preferable. On the contrary to the silver metallic electrode, where only the monolayer stripping peak of lead can be used for ASV determination of low lead concentration in only very short concentration interval (10^{-9} to 10^{-8} mol.L^{-1}), in the case of composite silver electrode only one anodic peak is applicable for the determination of lead in a wide concentration range (10^{-9} to 10^{-6} mol.L^{-1}).

A few different ways of repeatibility improving were tested (application of cleaning positive potential, cleaning cycles, etc.), but none of them was optimal. It is necessary to repeat each measurement more then three times, because according to the statistical test the first two records had to be omitted. For the evaluation is advisable to apply the median instead of arithmetic means (calculated from the third and subsequent measured records). Average relative standard deviation of measurements was about 1%, skewnest –0.5 to 0.5, excess 2.1 to 3.5.

3. Determination of Lead in Water Samples by DPASV

The samples of natural waters contain the traces of metal ions and usually also traces of surface-active organic substances. The influence of simultaneous deposition of copper, cadmium, and lead ions therefore was examined first by cyclic voltammetry at higher metal ions concentration (25 mg.L^{-1}). The obtained results showed that in 0.1 *M* $HClO_4$ and 0.05 *M* KCl electrolyte cadmium(II) ions yielded no cathodic or anodic response and did not influence the response of lead(II) ions, and on the other hand the presence of copper(II) ions resulted in the lowering of the stripping peak of lead situated at the more negative potential (Figure 9). It can be concluded that the simultaneous deposition of lead and copper does not influence the stripping of the monolayer of lead but strongly influences the anodic dissolution of the bulk deposit, the reason for this phenomenon is most probably the structure of the deposited mixture copper – lead.

From an analytical point of view, the examination of the influence of copper, cadmium, and other metal ions on the DPASV response obtained at the determination of low amounts of lead is more important. The results of DPASV showed that the anodic current of the more positive peak (monolayer) increased linearly with lead(II) ions concentration. The dependences of this anodic current were recorded with increasing lead(II) ions concentration (in the range from 50 to 500 ppb) and in the presence of 250 ppb of another examined metal ion. Under these conditions the linear dependences of the anodic current vs. lead(II) ions concentration were found. The presence of other metal ions in the measured solution changed only the slope of the linear dependence; this change corresponded to a lowering of the slope value by approx. 10 to 15% of the original value.

The influence of the presence of surface-active substances on the DPASV response of lead was also examined because natural water samples contain low amounts of surface-active organic substances. The DPASV measurement of lead at the concentration level tens of μg.L^{-1} showed that Triton X-100 up to concentration 5.10^{-4} % had no measurable effect on the results of the determination. These results confirm the possibil-

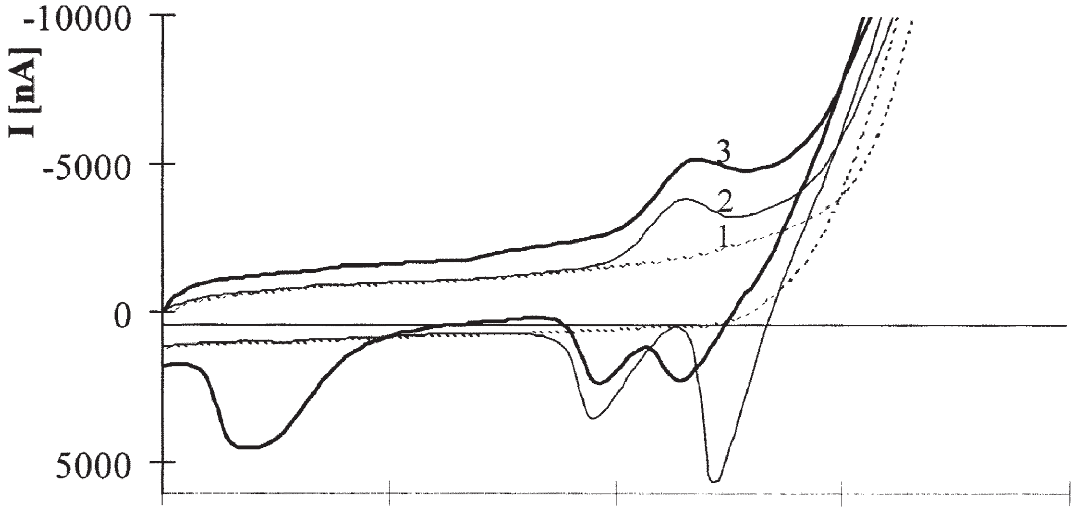

FIGURE 9. Cyclic voltammetry of cadmium(II), lead(II), and copper(II) in perchloric acid and potassium chloride electrolyte. Silver composite electrode, base electrolyte 0.1 *M* $HClO_4$ and 0.01 *M* KCl, scan rate 25 mV.s^{-1}, curve: (1) 20 mg.L^{-1} Cd(II), (2) 20 mg.L^{-1} Cd and 20 mg.L^{-1} Pb(II), (3) 20 mg.L^{-1} Cd(II), 20 mg.L^{-1} Pb(II), and 20 mg.L^{-1} Cu(II).

ity of the determination of low amounts of lead in natural water samples by DPASV using the composite silver electrode.

The trace amounts of lead thus were determined by DPASV using composite silver electrode in the tap water and river water samples. Twenty-three mililiters of the water sample was transferred into 25-ml volumetric flask and 0.5 ml of conc. $HClO_4$ and 1.5 ml of 1 *M* KCl solution were added, and the volume was diluted with water to 25 ml. The resulting solution was directly measured by DPASV using the parameters presented in Figure 10. The obtained results are in good agreement with the results obtained by DPASV determination carried out with hanging mercury drop electrode.

IV. CONCLUSIONS

The composite silver electrode has a wide analytical application. The preparation of this electrode is simple and easy. The surface of a freshly prepared electrode is simply brushed with emery paper, and the activation of the electrode surface is achieved by polishing and by cyclic voltammetry. The activation of a frequently used electrode is realized simply by repeated cyclic polarization every day before the measurement. The reproducibility of the results is improved by keeping the electrode potential at a definite value for a definite time interval before each measurement. Well-prepared electrode has long-term stability; it can be used for every day measurements without mechanical treatment of the electrode surface for at least 1 month. Compared with metallic silver electrode the preparation of the composite electrode is simple and economically more acceptable; the electrode has a very good stability and the activation of the surface is easy.

The effect of UPD observed at higher metal ions concentrations (10^{-4} mol.L^{-1}) in acidic electrolytes is identical to the UPD observed at metallic silver electrode. At lower lead(II) ions concentrations (10^{-9} to 10^{-6} mol.L^{-1}) in the presence of chloride ions only the monolayer stripping peak of the

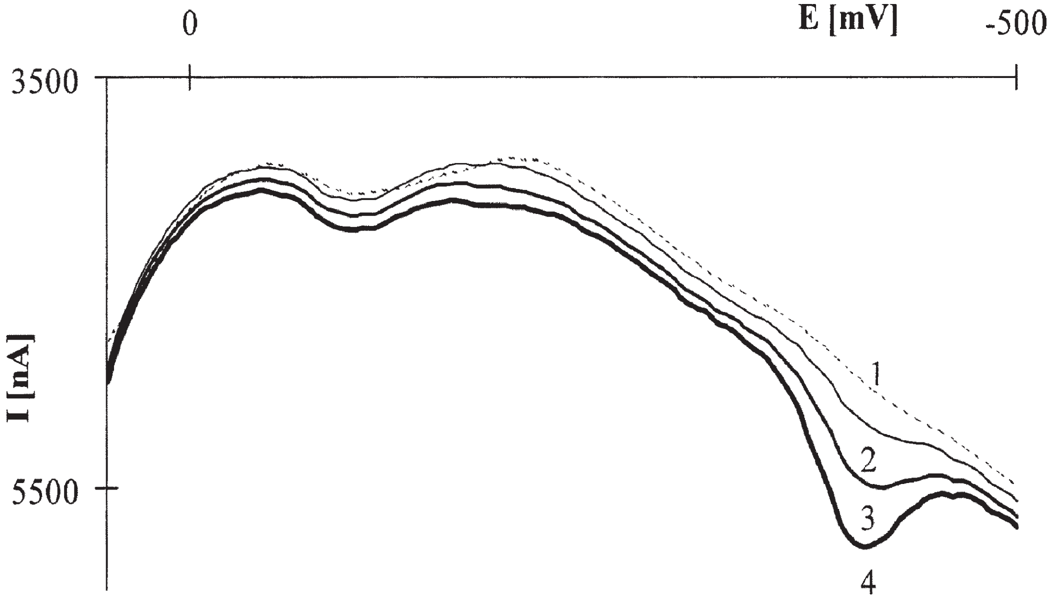

FIGURE 10. DPASV determination of lead in river water. Silver composite electrode, base electrolyte 0.1 *M* $HClO_4$ and 0.01 *M* KCl, deposition potential –0.85 V, deposition time 300 s, rest time 5 s, scan rate 20 mV.s^{-1}, curve (1) blank, curve (2) 23 ml of the water sample, 0.5 ml of conc. $HClO_4$, 1.5 ml of 1 *M* KCl), curve (3) and (4) standard additions 0.05 μl containing 0.5 μg lead(II).

deposited lead was observed, the bulk stripping peak was measured only at higher lead(II) ions concentration or at a long deposition time, the anodic current of this peak reached maximum 10% of the height of the monolayer peak.

Using this electrode it is possible to determine trace amounts of lead in natural water samples without the removal of dissolved oxygen and without the elimination of organic surface active substances presented in the sample. This electrode is also suitable for the determination of nitrate ions in natural water samples.

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