ANODIC STRIPPING VOLTAMMETRY USING GRAPHITE COMPOSITE SOLID ELECTRODE

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Dedicated to the memory of Professor Jaroslav Heyrovský on the occasion of the 50th anniversary of the Nobel Prize for polarography.

A graphite (carbon) composite solid electrode, prepared from graphite powder and epoxy resin, was used as a working electrode for anodic stripping voltammetry. The underpotential deposition effect, which appears at metallic electrodes, was clearly observed on this type of electrode as well. In the case of a simultaneous deposition of two metals on the surface of the composite solid electrode, the anodic dissolution of the metal, which is anodically dissolved at more negative potentials, is substantially influenced by the presence of the other deposited metal. This effect was exploited for the determination of lead in the presence of other metals by differential pulse anodic stripping voltammetry. The article presents possible applicability of such a type of very simple composite electrode to studies of the underpotential deposition effect as well as for analytical purposes.

Keywords: Graphite composite solid electrode; Voltammetry; Metals; Lead; Underpotential deposition effect; UPD effect; Electrochemistry.

As mentioned in the paper[1], devoted to the possibilities of utilization of silver composite solid electrode for anodic stripping voltammetry (ASV), the underpotential deposition (UPD) effect[2] was also observed when the composite solid electrode was prepared only from graphite powder and one insulating component (epoxy resin).

Composite solid electrode can be classified in several ways. The "classical" scheme was introduced about twenty years ago[3,4], the more detailed one was published recently[5]. The composite solid electrodes discussed in the following paragraphs, belong to the group of composite electrodes with

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randomly dispersed two components at least, which are solid after mixing. The electrodes are, with the exception of consistency, analogous to carbon paste electrodes (CPE)[6,7]. The composite solid electrode is defined as consisting of at least one conductor phase and at least one insulator phase[3,4]. The content of conducting phase can be expressed directly in the name (abbreviation) of the graphite (carbon) composite electrode (CCE), e.g. "CCEX" was prepared from *X*% of graphite powder and (100 – *X*)% of epoxy resin[5]. Composite solid electrodes offer certain advantages over metallic or glassy carbon electrodes (consisting of one conducting phase only), e.g. a lower cost, low weight, high signal-to-noise ratio, and the possibility of chemical modification of the conductor or insulator phase. The electrodes are more similar to metallic composite electrodes, which have been intensively studied in the recent years (e.g. silver[5,8–13] or gold[14] composite electrode).

The first graphite (carbon) composite electrode was already prepared by Adams about fifty years ago. This electrode had the form of a paste, which consisted of graphite powder and tribromomethane[15]. The preparation of this type of electrodes, based on graphite powder and an insulator is very easy, inexpensive and these electrodes could be very easily miniaturized. This type of electrodes can be applied not only *in vitro*, but *in vivo* as well (e.g. for electroanalysis of neurotransmitters[16]). The microelectrodes, consisting of two phases (graphite and epoxy resin in a disk ca. 25 μm in diameter) are suitable for measurements in organic solvents. They are characterized by a high signal-to-noise ratio[17]. CCEs have been also applied in voltammetric determination of inorganic (e.g. Mn) as well as organic substances (e.g. Alizarine Chrome Black PT, nitro and amino compounds, amino acids, adenine, guanine, phenylglyoxylic acid, etc.)[5,9,18–20].

In most literature sources it is reported (e.g. ref.[2]) that the UPD effect is weak and its voltammetric signals less reproducible on graphite particles of the electrode. Therefore, considering the influence of the UPD effect (e.g. refs[2,21–27]) on the voltammetric behavior of metal ions, the aim of the present work has been the study of simultaneous deposition and dissolution of several metals using CCEs. The authors' intention has not been concentrated on the study of the UPD effect on CCEs, but the aim was to report some potential analytical applications. A selected group of metals (Pb, Cd, Cu, Tl and Bi) was studied and their interactions on the electrode surface were described in detail. This paper is focused on studies realized using a CCE, while most of the paper on this topic so far published have been devoted to the study of the UPD effect and its analytical applications on solid monocrystalline or polycrystalline electrodes (e.g refs[21–27]) on screen-

printed electrodes[28] or on metal-plated rotograved carbon electrodes[29], i.e. on purely metallic materials (Au, Ag). This topic seems to be very complicated because of the complexity of the system in the presence of at least two different cations. Both metals can be adsorbed on the CCE surface, and they can also adsorb on each other. In principle, this can result in four different monolayer peaks. Beside them, of course, there are two bulk peaks of the two metals, not to speak of possible alloy depositions, formation of compounds in an intermediate oxidation state and effects of possible hydrogen deposition. Therefore, we tried to study and describe some of these effects associated with the use of CCE.

EXPERIMENTAL

Apparatus

The voltammetric measurements were performed using a computer-controlled voltammetric analyzer Eco-Tribo Polarograph equipped with Polar.Pro v. 5.1 software for Windows XP v. 5.0 (both Polaro-Sensors, Prague, Czech Republic). The controlling software was drawn up particularly for electrode pretreatment by the "Design" utility (included in Polar.Pro 5.1 software).

An Ag|AgCl (1.0 M KCl) electrode (separated by a salt bridge filled with saturated $NaNO_3$ solution) was used as a reference and a platinum wire as a counter-electrode. Nitrogen (99.99%) was used for the removal of dissolved oxygen from measured solutions.

The cell and the glass implements were cleaned with chromsulfuric acid and washed thoroughly with bidistilled water (conductivity < 1 μS cm^{-1}). All measurements were carried out at room temperature.

Reagents and Materials

An insulating component of the composite electrode was the epoxy resin Ceys which is based on Bisphenol A and epichlorhydrin, 80–92%; 1,4-bis(2,3-epoxypropoxy)butane, 3–9%; *n*-[3-(dimethylamino)propyl]propane-1,3-diamine (Ceys, S.A., Barcelona, Spain). The graphite powder used was an extra pure graphite (Merck, Ltd., Prague, Czech Republic), with particle size below 50 μm.

Standard solutions of metals were prepared by dilution of solutions containing 1 g l^{-1} of the metal in 2% HNO_3 v/v of analytical purity grade (Analytica, Ltd., Prague). All other chemicals used were of analytical purity grade. For all dilutions, bidistilled water of conductivity < 1 μS cm^{-1} was used.

Construction and Characterization of the Graphite Composite Solid Electrode

The electrode body was built from a 90-mm Perspex tube, with 12-mm outer diameter and 1-mm inner diameter. The graphite composite electrode CCE30 was prepared from graphite powder (70% (m/m)) and epoxy resin (Ceys) (30% (m/m)). The graphite powder was mixed with an epoxy resin and homogenized, and after ca. 5 min., the paste formed was pressed with a spatula into the electrode body; the polymerization (s.c. "curing") took ca. 6 h (ref.[5]).

Filling the inner part of the electrode body with graphite powder, into which a copper wire (2-mm diameter) was inserted, made the electric contact. The electrode was then brushed with emery paper of decreasing granulity, and in the end, it was gently polished with alumina paste (0.03 μm).

The electrode surface was activated by cyclic polarization (ca. 100 cycles with the scan rate 0.500 V s^{-1} in the potential window of the used base electrolyte (the voltage limits of this window correspond to the current of 1 μA). The frequently used electrode was regenerated by repeated cyclic polarization every day, before the measurement (approx. 50 cycles in the used supporting electrolyte). Electrodes prepared in this way can be used for everyday measurements for 3 or 4 weeks without any necessity of mechanical treatment of the electrode surface (only the above described cyclic polarization is sufficient).

The electrodes were stored in the air and their signal was tested using the standard solution of Pb(II) ions in various time intervals (1 day to 1 month). It can be concluded that the electrode surface is not influenced by air. The above mentioned cycling of the electrode removes all adsorbed particles.

The conditions for differential pulse anodic stripping voltammetric (DPASV) measurements were as follows: pulse amplitude 0.025–0.090 V, pulse width 100 ms, interval between pulses 200 ms, scan rate 0.025 V s^{-1} and 5 s long rest time period at the deposition potential without stirring[5].

The structure and morphology of the graphite composite electrode CCE30 were studied using scanning electron microscopy (SEM)[18]. It is quite difficult to obtain micrographs due to problematic differentiations between active (graphite) and inactive (epoxide) regions by optical microscopy.

The range of working potentials of the studied composite electrode was published in refs[5,18] for various base electrolytes: 0.1 M $HClO_4$, 0.1 M HCl, 0.1 M acetate buffer, 0.05 M borax buffer and 0.1 M NaOH. Only HCl, $HClO_4$ and acetate buffer solutions were further used in our experiments. The widest potential window was obtained in borax buffer (almost 4 V), which enables to use this CCE in the anodic as well as in cathodic region. For simplicity and to prevent undesirable, more complex influences of buffer components on metal deposition, the simplest, Clark–Lubs (HCl/KCl) buffer was used in our experiments. Only strictly defined solutions were studied. pH value of every analyzed sample was checked.

RESULTS AND DISCUSSION

Cyclic Voltammetry

The results obtained by cyclic voltammetry using a graphite composite electrode CCE30 showed that Pb(II) ions in 0.1 M $HClO_4$ produce two anodic peaks at the potentials –0.31 and –0.47 V, and a cathodic sigmoidal response at the potential –0.35 V (Fig. 1). During the anodic polarization, the three-dimensional (bulk) layer of deposited lead was stripped off at the potential –0.47 V (Fig. 1, peak Pb_b) and the monolayer at the potential –0.31 V (Fig. 1, peak Pb_m).

Only the signal corresponding to the deposition of lead monolayer at the potential –0.35 V appeared during cathodic polarization, because the cathodic signal corresponding to bulk deposition was overlapped by catalytic reduction of hydrogen ions. The catalytic reduction of hydrogen ions occurs at –0.81 V (out of the range of Fig. 1). If the influence of hydrogen ions was minimized by measurements in acetate buffer solution (pH 4.6), two cathodic sigmoidal signals and two anodic peaks were obtained as follows from the UPD effect, similarly as on the silver composite electrode[1].

The cathodic signals exhibit the shape of sigmoidal wave up to relatively high scan rates (see Fig. 1). Some authors explain this effect as follows: the composite electrode with the random distribution of active particles can be seen as array of microelectrodes, on which sigmoidal signal shapes are recorded[3,10,30,31]. On the contrary, the shapes of the anodic signals exhibit mostly the peak shape. The parameters of the monolayers peaks (ΔE_p, underpotential shift; $\delta_{1/2}$, half-peak width) by formation and dissolution have been often studied (e.g. in ref.[2] for metals, in refs[1,8] for metallic composite solid electrodes). They are determined by the electrode material (the narrowest peaks were recorded at monocrystalline, the widest on polycrystalline electrodes[1]). The half-width in the case of the metallic composite solid electrodes lies between these limits[10]. The half-width of the anodic monolayer peak on solid CCE amounted to more than 50 mV. This value is

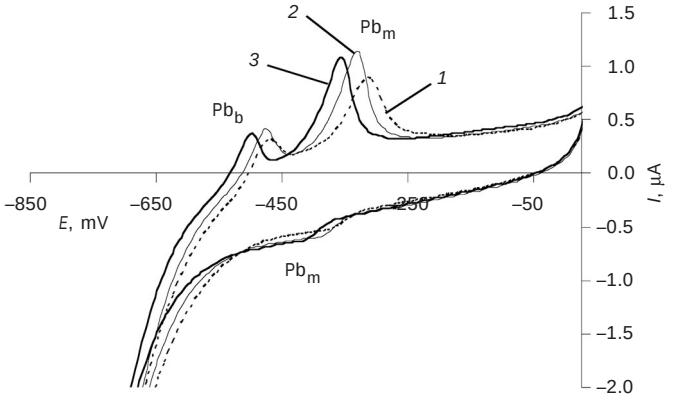

FIG. 1
Cyclic voltammograms of Pb(II) ions in various supporting electrolytes. CCE30, in the absence of oxygen, scan rate 0.050 V s^{-1}, 20 mg l^{-1} Pb(II). Peaks of lead: Pb_m, monolayer; Pb_b, bulk. Base electrolytes: *1* 0.1 M $HClO_4$, *2* 0.1 M $HClO_4$ + 0.01 M KCl, *3* 0.02 M KCl

a bit higher than that recorded on polycrystalline metallic electrodes (45 mV)[2]. Nevertheless, the processes on CCEs have not been fully explained yet. There were published some possibilities of mathematic description of these effects (e.g. ref.[2]), nevertheless, practically all of them are purely formalistic and do not involve all the paremeters: influencing metal ions concentration, nature of the electrolyte, specific interaction occurring between the electrolyte and the solid phase, etc.

The differrence in parameters of peaks corresponding to the monolayer formation and dissolution are given by different physical and chemical processes (e.g. the processes are influenced by present halogen ions).

The cathodic bulk peak of lead in Fig. 1 cannot be seen, because it is fully overlapped, covered by electrolyte decomposition. In some other experiments described in this paper, anodic monolayer peak is overlapped by signals of other metals (e.g. Tl, Cu). The other reason, why the bulk peak of lead cannot be registerred, consists in low concentration of lead in the analyzed solution. The bulk layer starts its formation yet after "complete" monolayer covering of the electrode surface (about 20% of active sites on the electrode surface, this value increases in presence of halide ions). If the concentration of the deposited metal is too low, the bulk peak cannot be

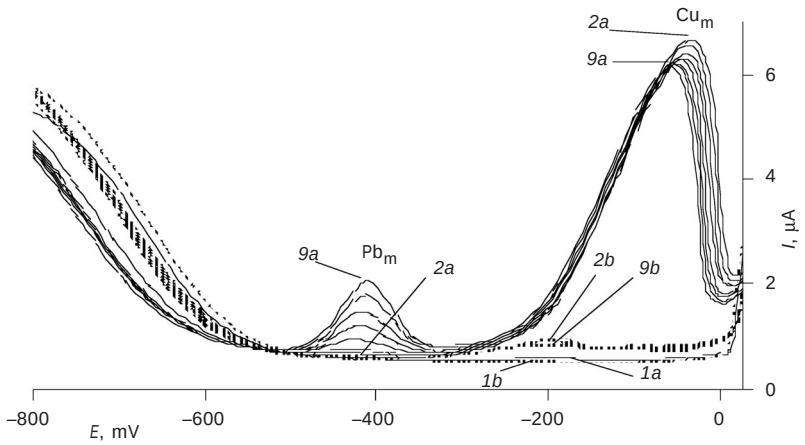

FIG. 2

DPASV of Pb(II) ions in the presence of Cu(II) ions. CCE30, supporting electrolyte 0.1 M KCl + 0.008 M HCl, in the absence of oxygen, E_{acc} = –0.850 V, scan rate 0.025 V s^{-1}, one cleaning cycle (from –0.850 to –0.050 V and back). t_{acc}: *a* 180 s (solid lines), *b* 0 s (dashed lines). Peaks: Pb$_m$, monolayer peak of lead; Cu$_m$, monolayer peak of copper. *1* Base electrolyte, *2–9* Cu(II) 2.4 mg l^{-1}. Pb(II) ion concentrations (in μg l^{-1}): *2* 0, *3* 12.5, *4* 25.0, *5* 50.0, *6* 75.0, *7* 100.0, *8* 125.0, *9* 150.0

registered at all or its height is not directly proportional to its concentration in the sample[8].

Figure 1 illustrates also the influence of chloride ions on the cyclic voltammetry of Pb(II) ions. The presence of chloride ions shifts both cathodic and both anodic peaks of lead to the region of more negative potential values. The differences of the potential values of the anodic bulk and monolayer peaks of lead – underpotential shift[2] (ΔE_p) – have a value of 0.158 V in the absence of chloride ions and of 0.143 V under identical conditions in the presence of chloride ions. These values differ substantially from those obtained using a silver composite solid electrode[1], where the underpotential shift decreased from 0.18 to 0.10 V due to the presence of chloride ions. The described results confirmed that the adsorption of chloride ions substantially decreased on the graphite composite solid electrode compared with the silver metallic or silver composite solid electrode.

Anodic Stripping Voltammetry of Lead

If differential pulse anodic stripping voltammetry (DPASV) of lead was performed in the supporting electrolyte 0.1 M KCl + 0.01 M HCl using graphite composite solid electrode, the response was represented by one monolayer peak and one bulk peak of lead at the potentials –0.43 and –0.54 V, respectively. The linear dependence of the peak current of monolayer as well as bulk peaks on the lead ion concentration was obtained applying the accumulation time t_{acc} = 180 s and the accumulation potential E_{acc} = –0.85 V. The linearity was proved in the range from 25 to 150 μg l^{-1} with the slope 1.05 nA l μg^{-1} in the case of the monolayer peak and from 50 to 350 μg l^{-1} with the slope 1.91 nA l μg^{-1} in the case of the bulk peak. These results fully corresponded to the presumption of the existence of the UPD effect at solid CCE.

Influence of Cu(II) Ions on ASV of Lead

Due to a small difference between the potential values of the anodic bulk and monolayer peaks of lead, the measurement of the mentioned peak heights is somewhat complicated. Therefore, the influence of Cu(II) ions on the nature of anodic voltammetric curves of lead(II), which is well known at silver composite solid electrode, was examined.

The results of cyclic voltammetric measurement of Pb(II) ions in the presence of the same concentration of Cu(II) ions have shown a decrease in the anodic bulk peak and an increase in anodic monolayer peak of lead. This

result is more obvious in DPASV measurement, where the deposition of copper on the electrode surface is more pronounced. Thus, it can effectively influence the deposition and dissolution processes of Pb(II) ions.

At the concentration 100 μg l^{-1} of Pb(II) ions, the anodic monolayer peak of lead (E_p = –0.43 V), measured by DPASV, increases linearly with increasing Cu(II) ion concentration (from 0 to 100 μg l^{-1} with the slope 0.27 nA l μg^{-1}), while the anodic bulk peak (E_p = –0.59 V) decreases linearly to zero value with the slope –0.72 nA l μg^{-1}.

More distinct is the influence of Cu(II) ions on the DPASV response to Pb(II) ions present at a very low concentrations. Figure 2 demonstrates the influence Cu(II) ions (2.4 mg l^{-1}) on DPASV of Pb(II) ions in the concentration range from 0.3 to 150 μg l^{-1}, in a mixture of 0.1 M KCl + 0.008 M HCl supporting electrolyte applying the t_{acc} = 180 s. It is evident from this experiment that monolayer peak of lead increases with the increasing concentration of Pb(II) ions linearly in the range from 10 to 150 μg l^{-1} (slope 9.51 nA l μg^{-1}). The bulk peak under these conditions disappears.

During the increase in the Pb(II) ion concentration, the height of the anodic monolayer peak of copper is not constant. A significant influence of lead deposition on the DPASV response of copper is shown in Fig. 3, which presents the dependence of the peak height of the anodic monolayer peak of copper (2 mg l^{-1}) on the t_{acc} in the presence of Pb(II) ions in the range from 0 to 200 μg l^{-1}. It is evident that the described effect of Pb(II) ions is limited in the concentration range up to 50 μg l^{-1}. A further increase in the

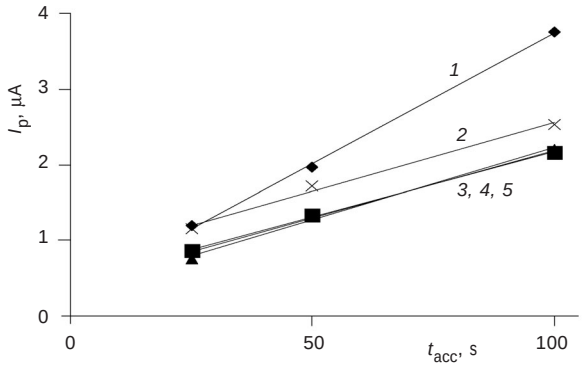

FIG. 3

Dependences of DP anodic monolayer peak current of copper on t_{acc} in the presence of Pb(II) ions. CCE30, base electrolyte 0.1 M KCl + 0.01 M HCl, in the absence of oxygen, E_{acc} = –1.000 V, scan rate 0.025 V s^{-1}, three cleaning cycles (from –1.300 to –0.050 V and back). Cu(II) ion concentration 2 mg l^{-1}. Pb(II) ion concentrations (in μg l^{-1}): *1* 0.0, *2* 25.0, *3* 50.0, *4* 100.0, *5* 200.0

Pb(II) ion concentration did not influence the monolayer peak of copper and its height remained practically constant.

It is evident from Fig. 2 that the height of the anodic signal of copper (monolayer peak at –0.04 V) is much lower than the signal of lead obtained at the same concentration. If, for example, the concentration of Cu(II) ions is 24 times higher than that of Pb(II) ions (100 μg l^{-1} Pb(II) and 2.4 mg l^{-1} Cu(II)), the anodic monolayer peak of copper is only 6 times higher than the anodic monolayer peak of lead. Therefore, the sensitivity of the determination to Cu(II) ions is much lover than to Pb(II) ions.

The influence of Cu(II) ions on DPASV response of Pb(II) ions was further examined in 0.1 M KCl as supporting electrolyte, because a higher pH value makes possible to record an interesting peak, the occurrence of which is associated with the presence of copper and which occurs in a more negative potential region. DPASV measurements realized in this electrolyte containing Cu(II) ions in the concentration range from 1 to 5 mg l^{-1} applying t_{acc} = 180 s are presented in Fig. 4.

Under the described conditions, Cu(II) ions yield the anodic monolayer peak at the potential –0.10 V (slightly shifting with increasing concentration of Cu(II) ions to more positive values; this shift is not caused by an increase in the H^+ ion concentration, pH was maintained constant). The other anodic peak was recorded at the potential –0.94 V (underpotential shift $\Delta E_p \cong 0.84$ V). This more negative peak increases linearly with increasing Cu(II) ion concentration (slope 0.52 nA l mg^{-1}). The anodic monolayer peak increases linearly only in the range up to 2.5 mg l^{-1} Cu(II) (slope 0.65 nA l mg^{-1}). The explanation of the more negative peak is more complicated. This peak cannot be formed by a simple dissolution of bulk copper, because Cu cannot be dissolved in neutral solutions at –0.94 V (vs Ag|AgCl). Copper is a much more noble metal than lead. The nature of the peak is under investigation. Nevertheless, for this text, for description of its character we used the preliminary, inaccurate term “bulk” peak of Cu(II), Cu_b.

In 0.1 M KCl medium, the influence of Cu(II) ions on the DPASV response of Pb(II) ions (see Fig. 4) is identical to that obtained in a more acid medium, but the sensitivity of the signal is lower. Under identical conditions, the slope of the linear dependence of the lead monolayer dissolution peak height on the Pb(II) ion concentration (5–100 μg l^{-1}) amounted to 4.26 nA l μg^{-1} (9.55 nA l μg^{-1} in the KCl/HCl medium). With linear increase of the Pb monolayer peak in dependence on Pb(II) ion concentration, the anodic monolayer peak simultaneously decreases like the “bulk” peak of copper. This decrease depends linearly on the Pb(II) concentration at longer

t_{acc}. The slope of the dependence of the monolayer peak height has the value –13.25 nA l μg^{-1} and that of the "bulk" –3.95 nA l μg^{-1} (t_{acc} = 180 s). Both copper anodic peaks diminish at shorter t_{acc}. Consequently, the simultaneous determination of Cu(II) and Pb(II) is a bit complicated on this electrode. The problem of lower sensitivity to Cu(II) ions is not essential, because the common concentrations of Cu(II) ions in water and biological materials are usually one or two orders of magnitude higher than those of Pb(II) ions.

The fact that anodic dissolution of the copper bulk layer is not as fast as the dissolution of the metal monolayer is shown in Fig. 5. The DPASV measurement was carried out in the following way: the anodic scan was realized first using t_{acc} = 180 s followed by short stirring for 2 s at the potential +0.02 V and immediately by the second anodic scan from –1.3 V, with no electrolysis time. It was found that at t_{acc} = 180 s the height of the anodic monolayer peak of copper increases linearly with the Cu(II) ion concentration ranging from 1.0 to 2.5 mg l^{-1} (slope 1525 nA l mg^{-1}). The peak height of the "bulk" peak increases also linearly in this concentration range (slope 412 nA l mg^{-1}). The slopes of these dependences, determined from the recorded curves with t_{acc} = 0 and 2 s after recording the first curve (Fig. 5), are 156.7 nA l mg^{-1} for the monolayer peak and 232.2 nA l mg^{-1} for the

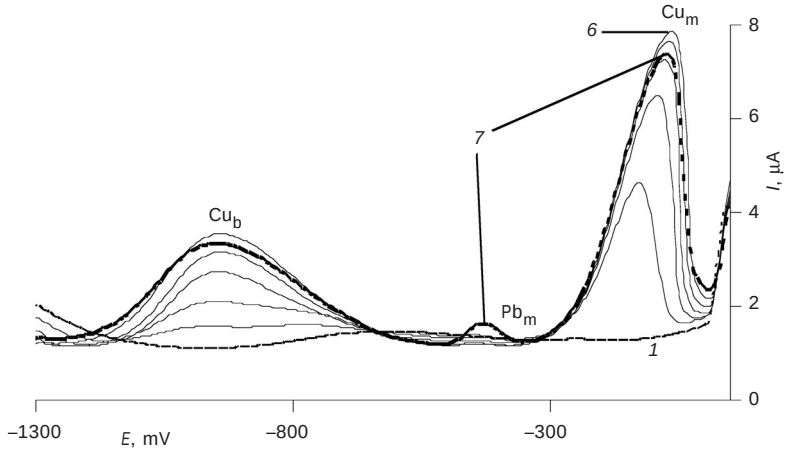

FIG. 4

DPASV of Cu(II) ions in the presence of Pb(II) ions. CCE30, base electrolyte 0.1 M KCl, in the absence of oxygen, E_{acc} = –1.000 V, scan rate 0.025 V s^{-1}, three cleaning cycles (from –1.300 to –0.050 V and back), t_{acc} = 180 s. Peaks: Pb$_m$, monolayer peak of lead; Cu$_m$, monolayer peak of copper; Cu$_b$, "bulk" peak of copper. Cu(II) ion concentrations (in mg l^{-1}): *1* 0.0, *2* 1.0, *3* 2.0, *4* 3.0, *5* 4.0, *6* 5.0, *7* 5.0 + Pb(II) 50 μg l^{-1}

"bulk" peak. These results demonstrate that at the zero time of electrolysis the copper monolayer peak decreases to 6% of the height obtained using t_{acc} = 180 s, while, under the same conditions, the "bulk" peak height decreases to 50% of the original height (Table I).

TABLE I
Dependence of "bulk" and monolayer anodic peak currents of copper on the accumulation time, Cu(II) ion concentration 1 mg l^{-1}

"Bulk"/monolayer peak	Accumulation time s	Peak current nA	Relative peak height, %
Mono	180	3693	100
Mono	0	219	6
"Bulk"	180	327	100
"Bulk"	0	162	50

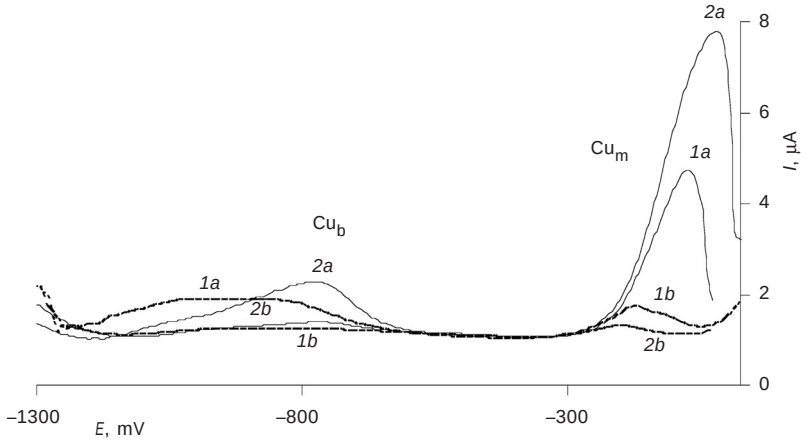

FIG. 5
Influence of t_{acc} on DPASV response of Cu(II) ions. CCE30, base electrolyte 0.1 M KCl, in the absence of oxygen, E_{acc} = –1.000 V, scan rate 0.025 V s^{-1}, three cleaning cycles (from –1.300 to –0.050 V and back). Peaks of copper: Cu_m, monolayer; Cu_b, "bulk". t_{acc}: *a* 180 s, *b* 0 s. Cu(II) ion concentrations (in mg l^{-1}): *1* 1, *2* 2.5

DPASV Determination of Lead in Presence of Other Metals

If the ASV determination of lead is realized in the presence of a metal deposited electrochemically together with lead at a negative potential, and if anodic dissolution occurs at a more negative potential than anodic dissolution of lead (e.g. Cd, Tl), no effect of such metal on the response of lead is observed. By ASV measurement of very high concentrations of Cd(II) ions (3 mg l^{-1}) and Pb(II) ions (50–175 μg l^{-1}) in 0.1 M KCl solution, only the anodic peak of cadmium at –0.75 V (Fig. 6, peak Cd_m) appears together with the bulk peak of lead at –0.53 V (Fig. 6, peak Pb_b) and monolayer peak of lead at –0.40 V (Fig. 6, peak Pb_m), i.e., the anodic dissolution of lead starts at the potential, at which the deposited Cd is already anodically dissolved.

The measurement of the ASV response of lead in the presence of Cd is more advantageous at higher H^+ concentration, e.g. of 0.1 M KCl + 0.1 M HCl, where the lead bulk peak is better separated from the cadmium peak. The effect of the presence of a high concentration of Cu(II) ions on the DPASV response of lead(II) in the presence of cadmium ions is the same as described above (increase the monolayer peak of lead).

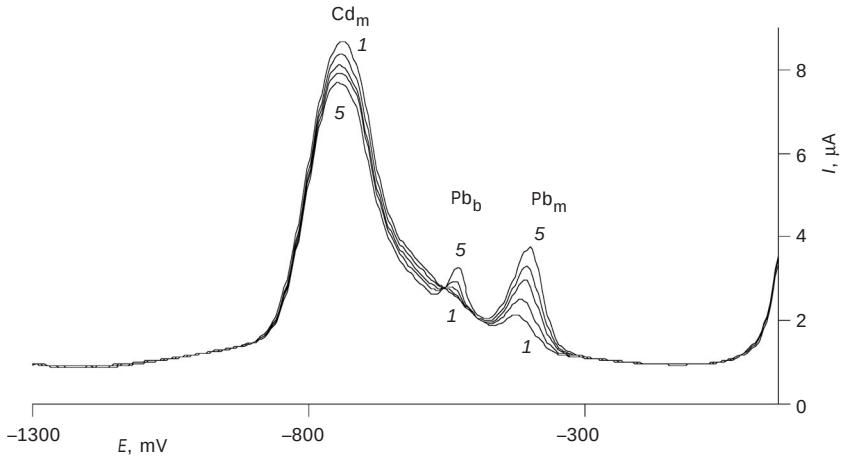

FIG. 6

DPASV of Cd(II) ions in the presence of Pb(II) ions. CCE30, base electrolyte 0.1 M KCl, in the absence of oxygen, E_{acc} = –1.000 V, scan rate 0.025 V s^{-1}, three cleaning cycles (from –1.300 to –0.050 V and back), t_{acc} = 180 s. Peaks: Pb_m, monolayer peak of lead; Pb_b, bulk peak of lead; Cd_m, monolayer peak of cadmium. Cd(II) ion concentration 3.0 mg l^{-1}. Pb(II) ion concentrations (in μg l^{-1}): *1* 50, *2* 75, *3* 100, *4* 125.0, *5* 175.0

Influence of Tl(I) Ions on ASV of Lead

In the electrolyte used (0.1 M KCl + 0.01 M HCl), the DPASV response of Tl(I) ions under the described conditions gives an anodic monolayer peak at the potential –0.61 V. At a higher concentration, also a bulk peak at the potential –0.86 V can be registered. In the concentration range of Tl(I) ions from 50 to 1000 μg l^{-1}, the monolayer peak height (Fig. 7, peak Tl_m) increases linearly with increasing Tl(I) ion concentration with the slope 1.13 nA l μg^{-1}, and the bulk peak (Fig. 7, peak Tl_b) increases in the range from 500 to 1000 μg l^{-1} with the slope 0.35 nA l μg^{-1} (t_{acc} = 60 s). In the DPASV determination of lead in the presence of thallium, the anodic dissolution process of deposited lead is not influenced by the dissolution process of thallium, which occurs at more negative potential. However, due to a small difference between the bulk peak potential of lead and monolayer peak potential of thallium, the measurement of the peak heights is not exact enough. The influence of Cu(II) ions on the DPASV response of thallium is not very significant – a twenty times increase of Cu(II) ion concentration leads to an increase in the thallium monolayer peak height by

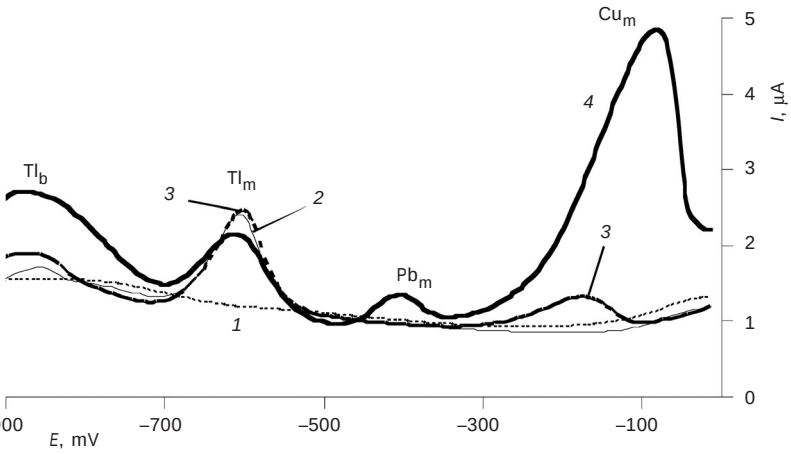

FIG. 7

DPASV of Tl(I) ions in the presence of Cu(II) ions. CCE30, base electrolyte 0.1 M KCl + 0.01 M HCl, in the absence of oxygen, E_{acc} = –1.000 V, scan rate 0.025 V s^{-1}, three cleaning cycles (from –1.000 to –0.050 V and back), t_{acc} = 60 s. Peaks: Pb_m, monolayer peak of lead; Cu_m; monolayer peak of copper; Tl_m, monolayer peak of thallium; Tl_b, bulk peak of thallium. Tl(I) ion concentrations (in μg l^{-1}): *1* 0, *2* 1000, *3* 1000 + Cu(II) 1000 μg l^{-1}, *4* 400 + Cu(II) 4000 μg l^{-1} + Pb(II) 200 μg l^{-1}

ca. 7% of the original height. As the bulk peak potential of copper is close to –0.90 V, also the bulk peak height of thallium (Fig. 7, peak Tl_b) increases with increasing Cu(II) ion concentration.

It follows from the presented curves that under the given conditions, it should be possible to record the ASV monolayer peak of lead (at the potential –0.41 V) even in the presence of thallium and copper. The voltammetric curve *4* presented in Fig. 7 confirms this conclusion. The obtained results confirm the linear dependence of the monolayer peak height on Pb(II) ion concentration in the range 50–500 μg l^{-1} in the presence of Cu(II) ions (4 mg l^{-1}) and Tl(I) ions (0.4 mg l^{-1}) with the slope 1.94 nA l μg^{-1} (t_{acc} = 60 s). It should be mentioned that the slope depends on the Cu(II) ion concentration: with decreasing Cu(II) concentration also the slope decreases; at the Cu(II) ion concentration 2.5 mg l^{-1} the slope decreased to 1.13 nA l μg^{-1} under the same experimental conditions.

Influence of Bi(III) Ions on ASV of Lead

DPASV of Bi(III) ions yields a not very well developed anodic monolayer peak at the potential –0.11 V and a bulk peak at the potential –0.85 V in the KCl/HCl solution. For the voltammetric determination of bismuth, the application of an acid supporting electrolyte is evidently more convenient. On the other hand, similarly as described above, the presence of Cu(II) ions also causes well acceptable conditions for the DPASV determination of lead in the medium containing Bi(III) ions. For the DPASV determination of lead in the presence of Bi(III) ions, the described method, based on the increase in the anodic monolayer of the Pb peak by simultaneous deposition of Cu(II) ions, can be applied. By the determination of lead in the concentration range from 50 to 500 μg l^{-1} in the presence of Bi(III) ions 0.5 mg l^{-1} and Cu(II) ions 2.0 mg l^{-1}, the dependence of the monolayer peak current of lead is linear with the slope 3.0 nA l μg^{-1} (Fig. 8, peak Pb_m).

Presence of Surface-Active Substances

The affection of DPASV determination of Pb(II) ions in the presence of the surface-active substances (SAS) was studied using the model substance – Triton X-100 (Fig. 9). A low concentration of Triton X-100 causes only a decrease in the height of the lead monolayer peak without any deformation. The presence of 1 mg l^{-1} of Triton X-100 causes a decrease in the peak height of 40% (the dependence of the peak height versus Triton X-100 concentration was practically linear up to that concentration), but a further

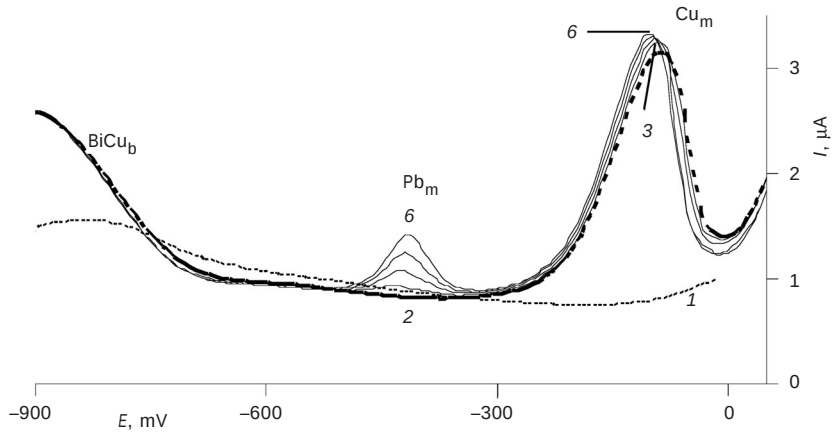

FIG. 8

DPASV of Pb(II) ions in the presence of Bi(III) ions. CCE30, base electrolyte 0.1 M KCl + 0.01 M HCl, in the absence of oxygen, E_{acc} = –1.000 V, scan rate 0.025 V s^{-1}, one cleaning cycle (from –1.000 to –0.050 V and back), t_{acc} = 60 s. Peaks: Cu$_m$, monolayer peak of copper; Pb$_m$, monolayer peak of lead; BiCu$_b$, "bulk" peaks of bismuth and copper. *1* Base electrolyte, *2–9* Bi(III) 0.5 mg l^{-1} + Cu(II) 2.0 mg l^{-1}. Pb(II) ion concentrations (in μg l^{-1}): *2* 0, *3* 50, *4* 100, *5* 150, *6* 200

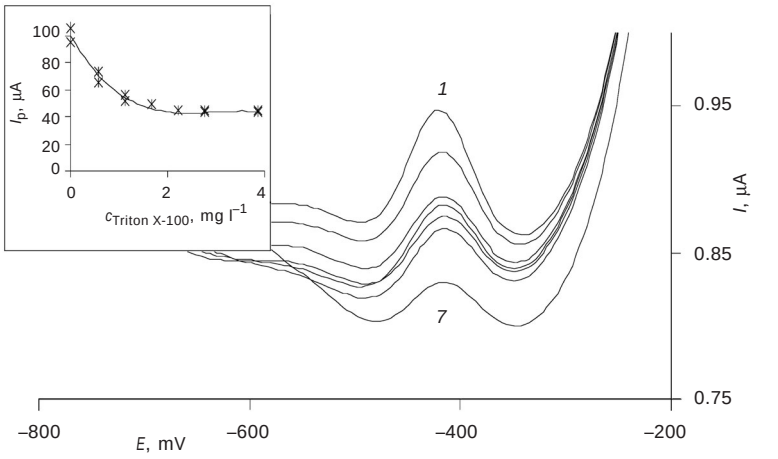

FIG. 9

Influence of Triton X-100 on DPASV of monolayer peak of lead. CCE30, base electrolyte 0.1 M KCl + 0.01 M HCl, in the absence of oxygen, E_{acc} = –1.000 V, scan rate 0.025 V s^{-1}, one cleaning cycle (from –1.000 to –0.050 V and back), t_{acc} = 180 s. Concentration of Pb(II) 200 μg l^{-1} + Cu(II) 1.5 mg l^{-1}. Concentrations of Triton X-100 (in mg l^{-1}): *1* 0.00, *2* 0.58, *3* 1.13, *4* 1.68, *5* 2.24, *6* 2.78, *7* 3.86. Inset: Dependence of DP anodic monolayer peak current of lead on the Triton X-100 concentration

increase in Triton X-100 concentration does not affect this parameter substantially (10% decrease in the range from 1 to 4 mg l^{-1} (see Inset in Fig. 9).

On the other hand, the monolayer peak current due to lead decreased in the presence of Triton X-100 (generally, any SAS). The concentration in the analyzed sample is constant, but it increases linearly with increasing Pb(II) ion concentration. It was verified that the use of the standard addition method eliminates the matrix effect in the determination of the lead, i.e., the result is not distorted by the presence of SAS.

Repeatability and Reproducibility

The graphite composite solid electrodes, like other solid electrodes, suffer from lower reproducibility and worse renewable surfaces in comparison with the mercury drop electrode. The repeatability was tested by twelve repeated measurements of the same solution of Pb(II) ions with addition of Cu(II) ions. In contrast to the silver composite solid electrode[1], all records could be involved in the calculation of the arithmetic mean (no point was extreme or outlaying). However, it is generally accepted that it is advisable to use for characterization the median instead of the arithmetic mean. Relative standard deviation (calculated from the above mentioned 12 measurements) amounted to ca. 2%; skewness from –0.5 to +0.5 and excess from +2.5 to +3.0. These results led us to the conclusion that the results are normally distributed.

The reproducibility was tested by determination of Pb(II) ions in the same standard solution in three different laboratories. The obtained results varied by 6.5%.

The repeatability and reproducibility of the results can be partly improved by repeated application of the appropriate electrochemical pretreatment (described in the paragraph Construction and Characterization of the Graphite Composite Solid Electrode), but the improvement is practically negligible.

The achieved reproducibility of the voltammetric measurement is acceptable and the experiments confirmed that the activity of the electrode surface remains constant even during a long time measurement without mechanical pretreatment of the electrode surface.

Determination of Lead in Water Samples

The analytical exploitation of the UPD effect recorded using CCE was tested on lead determination. To 10 ml of the analyzed sample, a proper support-

ing KCl/HCl electrolyte (final concentrations: 0.1 M KCl + 0.008 M HCl) was added. First, two model samples containing 50 and 25 μg l^{-1} of Pb(II) ions were analyzed under the above described conditions (t_{acc} = 180 s). A solution of Cu(II) ions was added to the sample to obtain their final concentration of 2 mg l^{-1}. The standard addition method was used to quantify the lead concentration. The following results (concentrations of Pb(II) ions) 49.70 ± 0.41 and 25.51 ± 0.72 μg l^{-1} were achieved (confidence intervals were calculated with the probability 95%).

Similarly, to 10 ml of freshly sampled tap water, the same supporting electrolyte (0.1 M KCl + 0.008 M HCl) was added, and the prepared solution was analyzed by DPASV under the above described conditions (t_{acc} = 180 s). To eliminate the possible matrix effect, the standard addition method was used to quantify the lead concentration. The obtained result was 6.45 ± 1.01 μg of Pb(II) ions in 1 l. The sample was also analyzed with the addition of cupric ions (2 mg l^{-1}), and the concentration 7.14 ± 0.84 μg l^{-1} of Pb(II) was obtained. The value 7.25 ± 0.42 μg l^{-1} was obtained by the measurement of the same sample using HMDE after removing the surface-active substances by microwave digestion. We can conclude that the confidence intervals of all results overlapped with the 95% probability and that the surface-active substances did not significantly affect the determination.

In the absence of copper in the sample, the following parameters were calculated: limit of decision 2.21 μg l^{-1}, limit of detection 3.09 μg l^{-1}; limit of determination 5.64 μg l^{-1}, and in the presence of copper in the sample limit of decision 1.90 μg l^{-1}, limit of detection 3.46 μg l^{-1}; limit of determination 5.12 μg l^{-1} (i.e., both the determined concentrations of Pb(II) ions in tap water were above the limits of determination). It can be concluded that the reachable limits of detection on CCEs are higher in comparison with mercury electrodes; nevertheless, they are sufficient according to the requirements for analysis of ecological samples (e.g. according to the valid standards for drinking water).

CONCLUSIONS

According to the presented and other previously published results, the graphite solid composite electrode, prepared from graphite powder and epoxy resin, is a suitable working electrode for anodic stripping voltammetry.

The preparation of such electrode is simple, easy and economically more acceptable in comparison with a metallic or a composite metallic (e.g. silver) electrode[5,9]. As the graphite solid composite electrodes do not contain any mercury, they present (as well as metallic composite[1,5,8,10–14,32], metal-

lic[26,33,34], solid amalgam and solid composite amalgam electrodes[9,35–39]) an acceptable electrode material in all analytical laboratories.

A well-prepared graphite composite solid electrode shows a long-term stability and its surface is not influenced by the air atmosphere. It can be used for everyday measurements without mechanical treatment of the surface for at least 3–4 weeks. During this time it is sufficient to perform 20 cycles in the chosen potential window at the scan rate 0.5 V s^{-1}.

The underpotential deposition effect, which appears at metallic and metallic composite solid electrodes, was also observed with this type of electrode.

The presented results show that in simultaneous deposition of lead and copper, the following anodic dissolution is somewhat complicated, compared with the dissolution of other metals, e.g. Pb–Cd, Cd–Cu, Pb–Tl and Pb–Bi. In the described DPASV measurements of solutions containing Cu(II) and Pb(II) ions, the results show an increase in the anodic monolayer peak height of lead and, simultaneously, a decrease in the anodic bulk peak height of lead with increasing Cu(II) ion concentration. The acceptable explanation of the effect is an increase in the lead deposition due to a change of the electrode surface quality. It can be expected that the CCE surface enables lead deposition on a certain part of the electrode surface. In the presence of Cu(II) ions (at higher concentration than that of Pb(II) ions), the quality of the electrode surface is changed, probably by copper deposition and, most probably, a larger surface area is formed, where higher amounts of lead can be deposited. This effect was experimentally confirmed by the fact that the monolayer peak of lead(II) increases and the bulk peak decreases with increasing copper(II) ion concentration.

According to presumptions and reported results, it is in accord with the hypothesis that during ASV of lead and copper, using the graphite composite solid electrode, lead is deposited on the monolayer of copper, formed before the start of the lead deposition. This assumption is confirmed by the fact that with the increasing concentration of Pb(II) ions at a constant concentration of cupric ions, the anodic monolayer peak of copper decreased whereas the anodic monolayer peak of lead increased.

Thallium is active on the graphite composite solid electrode in KCl/HCl electrolyte, yielding a monolayer as well as bulk peaks in the presence or absence of copper. The influence of Cu(II) ions on the DPASV response of thallium is not too significant.

In KCl/HCl solution, DPASV of Bi(III) ions yield a not well developed anodic monolayer and a bulk peak. In the same electrolyte, a high concen-

tration of Cd(II) ions yields, in the presence of Pb(II) ions, one anodic peak (probably monolayer).

Only the most important metals and their interactions on the electrode surface (in other words, most mutually influencing metals) were described in detail (Pb, Cd, Cu, Tl and Bi). A wide range of other metals (e.g. Zn(II), Mn(II), Co(II), Ni(II), Fe(III), As(III) and Se(IV)) does not affect the determination of lead in the presence of relatively high concentration of cupric ions.

Using this electrode, trace amounts of Pb(II) ions can be determined in the presence of other metals in natural water without removing small amounts of organic surface-active substances.

It is possible to conclude that the graphite composite solid electrodes can be utilized for study of underpotential deposition processes of metals as well as for analytical purposes.

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