Study of influence of various factors on electrochemical signal of lead in water solutions

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Abstract. The conditions for obtaining a reproducible signal of lead in water solutions of indifferent electrolytes on various substrates (working electrodes) for analytical purposes were studied. Attention was also paid to studying the regularities of the initial stage of formation of lead sediments by the method of inversion voltammetry. The possibility of using different working electrodes to obtain stable current-potential curves is shown depending on the conditions of electrolysis, pH of the medium, the electrolysis potential and impurities.

1. Introduction
The study of the processes taking place at the electrode and solution interface has received a lot of attention in recent decades [1-7]. This concerns both the issues of quantitative determination of elements in natural environments with the aim of increasing the sensitivity, and the development of methods for studying the initial stages of the formation of new phases.

The electrochemical useful signal is a curve with an acute maximum (Fig. 1).

![Figure 1](image-url)  
Figure 1. A general view of the polarization curve of the electrical dissolution of the lead plate. curve 1 – background line; curve 2 – peak of lead plate dissolution  
Background – 0.2M KCl, pH = 3.5, \( C_{Pb^{2+}} = 4.7 \times 10^{-5} \) mole/l; \( \tau_e = 2 \) min;  
\( E_s = -0.9V, \ w = 40 \) mV/s for a glassy-carbon electrode.
2. Materials and methods
Dependences for the peak-point currents of the process of electrical dissolution of plates concentrated on the glassy-carbon, copper and silver electrodes, on the concentration of the depolarizer, on the time of the electro-accumulation, on the electrolysis potential, and on the pH of the solution were obtained. The influence of various factors on the structure of the lead plate has been studied as well as the number of nucleating centers and their radius has been calculated. The effect of the adsorption of chloride and iodide ions on the process of the anodic dissolution of lead sediments concentrated on a silver electrode was studied.

The dependence of the peak-point current and the amount of electricity of anodic dissolution of the lead plate, electro-deposited on a glassy-carbon electrode from a 0.2M KNO₃ solution with pH = 2.75 on the concentration, was obtained. It was found that in the concentration range from 7.1*10⁻⁶ to 1.4*10⁻⁴ mole/l, the I-C and Q-C dependences had linear character, which could be used for analytical purposes. Deviation from linearity was observed at concentrations >1.4*10⁻⁴, when volumetric layers of the plate form on the electrode surface.

The dependence of the current and the amount of electricity of the anodic dissolution of the lead plate on the accumulation time (I-t, Q-t) has a similar nature, which is related to the amount of the plate on the electrode.

On the silver electrode in 0.2M KNO₃, during anodic dissolution of the plate, there are two peaks (Figure 2) with different potentials. At low concentrations or accumulation times, an adsorption peak (Eₚₙₐ=-0.28V) is registered, with increasing in concentration or accumulation time, a more electronegative, analytical peak appears (Eₚₐₜ=-0.44V), which is used in inversion voltammetry for quantitative and qualitative analysis.

![Figure 2](image.png)

**Figure 2.** A general view of the polarization curve of the electrical dissolution of the plate; curve 1 – background line; curve 2 – peak-point of lead plate.

The first peak-point is an analytical signal; the second peak-point is an adsorption signal.
Background = 0.2M KCl, pH = 3.5, \( C_{Pb^{2+}} = 4.7 \cdot 10^{-5} \) mole/l; \( \tau = 2 \) min; \( E_s = -0.9 \) V, \( w = 40 \) mV/s for a copper electrode.

Further, when studying the dependencies on various factors, let us deal with an analytical signal.
Dependences of anode peak-points on glassy-carbon, silver and copper anodes on the potential of electro-accumulation have been studied (Fig. 3, 4). These dependences come through the maximum, which is due to the hydrogen evolution, which reduces the current output of lead and blocks the surface for lead plate.

![Figure 3. Dependence of the current peak-point of lead plate dissolution (Curve 2) and the amount of electricity plate (Curve 1) on the electrolysis potential. Background – 0.2M KNO$_3$, pH = 3.5, C$_{Pb^{2+}}$ = 4.7 mole/l; $\tau_e$ = 2 min; w = 40 mV/s for a copper electrode.](image)

The optimum value of the potential of electro-accumulation at 0.2M KNO$_3$ on the copper electrode is in the range of -0.6V, and 0.2M KCl in the solution in the range from -0.9 to -1.2V. Considering the size and width of the anodic lead peak-point, the nature of the background affects the reversibility of the process. Because of the formation of complexes that affect the discharge energy, the shape of the peak (the width of the half-peak) changes.

Dependence of the current peak-point and the amount of electricity on the pH of the indifferent electrolyte was studied (Fig. 3). As the acidity of the solution increases, the dissolution current peak-point decreases due to the effect of the hydrogen evolution process. Optimal pH values of indifferent electrolyte for studying the physicochemical properties of the plate, as well as for analytical purposes on various electrodes, are:

- glassy-carbon electrode: pH= 3.75;
- silver electrode: pH= 3.5-3.7;
- copper electrode: pH= 3.0-3.5.
Figure 4. The number of lead sediment nucleating centers and their sizes from the electrolysis potential.

In order to study the structure of the lead plate, the experimental data were processed on the basis of the concepts of nucleation of plates developed in the papers [8, 9] with reference to the conditions of inversion voltammetry.

In the process of electrical dissolution of embryos, current-potential curves passing through the maximum are recorded. The magnitude of the current at any time is described by the equation:

\[ I = \frac{MN^2q^2z(\delta t)}{2} \]

\[ \bar{M} = n\bar{\gamma}C(D\delta)^{1/2} \]

\[ \bar{\gamma} = 2\pi\left(\frac{3M}{2F}\right)^{2/3} \]

\[ \bar{M} = \frac{M'}{nF\rho} \]

\[ \delta = \cdot w = \frac{hF}{RT}w \]

Here:
- \( M' \) – molar mass, g/mole;
- \( \rho \) – plate density, g/cm\(^3\);
- \( F \) – Faraday number, C/g-e;
- \( D \) – diffusion coefficient, cm\(^2\)/s;
- \( C^* \) – concentration of ions in the depth of the solution, mol/cm\(^3\);
- \( n \) – number of electrons participating in the electrode process;
\( N \) – number of nucleating centers on the electrode.

By equation 1, one can calculate the number of nucleating centers at any point of the polarization curve. The solution of equation 1 with respect to value \( J \) can be expressed by the function:

\[
X_m = \delta \cdot t_m, \tag{6}
\]

where \( t_m \) – half-peak width, s.

There were calculated function curves \( X_m \) of \( \lg \bar{\theta} \) in papers [27, 28], where:

\[
\bar{\theta} = nF\gamma C^0 N^{1/3} D^{1/2} \delta^{-1/2} q_0^{-1/3} . \tag{7}
\]

From the above-mentioned expressions, the number of nucleating centers on the electrode can be found:

\[
N^{1/3} = \frac{\delta^{1/2} q_0^{1/3} \bar{\theta}}{nF\gamma C^0 D^{1/2}}. \tag{8}
\]

The average size of nucleating centers \( r_m \) can be found from the expression:

\[
q_0 = \frac{4}{3} \pi r_m^3 \cdot N; \tag{9}
\]

\[
r_m = \frac{3q_0}{4\pi N}. \tag{10}
\]

Knowing the half-peak width, one can find function \( X_m \) by formula 6.

Under optimal conditions for the dependencies described earlier the number and size of the nucleating centers formed on the electrode were analyzed.

The dependence of number \( N \) (curve 1) and radius \( r \) of the nucleating centers (curve 2) for the glassy-carbon electrode in 0.2 M \( \text{KNO}_3 \) on the concentration was obtained (Fig. 5).

![Graph showing the dependence of number \( N \) and radius \( r \) on the concentration.](image)

**Figure 5.** Dependence of number \( N \) (curve 1) and radius \( r_m \) of the nucleating centers (curve 2) on the electrolysis potential. Background – 0.2 M \( \text{KNO}_3 \), \( \text{pH} = 3.5; \) \( C_{\text{Pb}^{2+}} = 4.7 \times 10^{-5} \) mole/l; \( \tau_e = 2 \) min; \( w = 40 \) mV/s. for a glassy-carbon electrode.

With an increase in the concentration, the lead plate growth occurs due to overlapping of nucleating centers into larger formations, while their radius increases and the number of embryos decreases.

Dependence of the number of nucleating centers and their radius on the time of electrical accumulation on a glassy-carbon electrode on the background 0.2 M \( \text{KNO}_3 \), containing 4.74 \( \times 10^{-5} \) mole/l, \( \text{pH} = 3.5; \) \( C_{\text{Pb}^{2+}} = 4.7 \times 10^{-5} \) mole/l; \( \tau_e = 2 \) min; \( w = 40 \) mV/s. for a glassy-carbon electrode.
Pb(NO$_3$)$_2$ shows that lead plate with an increase in time of electrolysis occurs due to the merging of crystallization centers into larger formations, which radius increases.

Dependence of the number of embryos as well as their radius deposited from 0.2M KNO$_3$ and 0.2M KCl on the potential of electrolysis was studied. The dependence of the number of nuclei passes through a maximum, and the dependence of the radius of the embryos on the potential of the electric accumulation passes through a minimum. The points of the maximum and minimum of the curves were observed at practically the same value of the potential of electro-accumulation. In the potential range, more positive than the maximum of the electrolysis potential, the plate growth occurs due to an increase in the number of nucleating centers on the surface of the electrode, and not at the expense of an increase in their sizes.

In the range of potentials, which is more negative than the maximum of the potential for accumulation, the growth of the sediment is mainly due to the fusion of nuclei into larger ones due to the fact that part of the electrode surface is blocked by evolved hydrogen.

The dependence of the number of nucleating centers and their dimensions on the nature of the electrolyte is shown. Thus, for example, the number of nucleating centers of lead deposited from 0.2M KCl is larger than that from 0.2M KNO$_3$. In both cases, the electrolysis was carried out under optimal conditions ($E_e$, pH, w).

The electrode material influences the nature of the plate. For example, on the glassy-carbon electrode, the number of nucleating centers is 2 times and the size is 1.5 times larger than those on the copper electrode, which is due to the difference in the substrate structure, the hydrogen overvoltage on these substrates, and also the structure of the double electric layer on the electrode surface as well as with the magnitude of the potential of zero charge.

The dependence of the number of nucleating centers $N$ and the radius of nucleating centers $r_m$ on glassy-carbon, copper and silver electrodes from pH of the solution on the background 0.2M KNO$_3$ is obtained. The growth of the lead sludge in the range of pH 6.8 – 4.0 is due to an increase in the number of nucleating centers. In the range of pH 3.5 – 2.13, the growth of the plate is due to the fusion of nucleation and the increase in their size, due to the fact that a part of the surface of the electrode is blocked by evolved hydrogen bubbles.

On a silver electrode, it was necessary to take into account the influence of impurity ions Cl$^-$ and I$^-$, since they are tension-active, and silver forms hardly soluble compounds with them. This especially applies to iodide ions. The experiment showed that at a concentration of an iodide ion, the useful signal, commensurate with the concentration of lead, decreased noticeably, which was due to the achievement of the solubility product. At similar concentrations of chloride ions, a decrease in the peak-point of lead was not observed. Only the iodide ion exerts a noticeable influence on the current peak-point of lead for a copper electrode under the same conditions. On the glassy-carbon electrode, the influence of impurity ions was much less.

3. Conclusion
1. The possibility of obtaining well-reproduced signals of anodic dissolution of lead plates for various electrodes is shown.
2. The effect of the nature of the background electrolyte on the magnitude of the useful signal is studied.
3. Dependences of the value of the useful signal on the electrolysis potential, on the electrolysis time, on the pH of the solution and on the nature of the substrate were obtained.
4. Dependences of the plate structure on the conditions of electrolysis are revealed.
5. Optimum conditions for obtaining a stable and well reproducible useful signal are found.

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