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APPLIED ELECTROCHEMISTRY
AND CORROSION PROTECTION OF METALS

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A Study of Adsorption of Lead, Cadmium, and Zinc Ions on the Glass Surface by Stripping Voltammetry

I. E. Stas', B. P. Shipunov, I. N. Pautova, and Yu. V. Sankina

Altai State University, Barnaul, Russia

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Abstract—Stripping voltammetry was applied to study the influence exerted by the brand of glass on the amount of adsorption of heavy metal ions from solution. The dependence of the amount of the adsorbed ions on their concentration in solution and on the concentration of the supporting electrolyte was analyzed.

The material from which laboratory glassware and vessels for storage of solutions are fabricated may be a source of contamination and a reason for a change in the concentration of solutions they contain [1]. The laboratory glassware is most frequently made of glass. Various brands of glass differ in the composition, chemical resistance, and sorption power [2]. It is known that the glass surface is charged negatively in aqueous solutions because of the surface dissociation of silanol groups [3]. Therefore, glass can adsorb cations.

To determine microscopic amounts of a substance, on the order of 10^{-7} M and less, stripping voltammetry (SVA) is widely used [4–6]. For this technique, changes in the concentration of elements to be determined, which occur as a result of adsorption–desorption processes, are important. This is so because, when working with concentrations of about $n \times 10^{-7}$ M, $n \times 10^{-9}$ mol of a substance is contained in a solution being analyzed (at a sample volume of 10–20 ml), whereas the adsorption of ions may be as high as $n \times 10^{-10}$ mol cm^{-2} [7]. However, no systematic studies of the adsorption of heavy metal ions, conventionally determined by SVA, on the glass surface and no comparative estimates of the adsorption capacity of various brands of glass have been performed.

The aim of this study was to examine the adsorption of lead, cadmium, and zinc ions on the glass surface by SVA at ion concentrations in solution of $n \times 10^{-7}$ M.

EXPERIMENTAL

The study was carried out using a PU-1 polarograph with two-electrode cells fabricated from various

brands of glass. A needle-like mercury-film electrode on a silver substrate ($S = 0.35 \text{ cm}^2$) served as indicator electrode, and a silver chloride electrode, as reference. Reference and supporting-electrolyte solutions were prepared using demineralized water and chemically pure reagents. As supporting electrolyte served 0.01 M KCl (pH 5.95). Reference solutions of the elements being studied were prepared by the known method [8]. The concentration of the elements to be determined in the solutions under study was $c_{\text{Pb}^{2+}} = c_{\text{Cd}^{2+}} = 4 \times 10^{-7}$, $c_{\text{Zn}^{2+}} = 9 \times 10^{-7}$ M. Dissolved oxygen was removed by bubbling preliminarily purified gaseous nitrogen through a solution. The same flow of nitrogen served to agitate ground glass (adsorbent).

Zinc, lead, and cadmium were accumulated on the electrode at a potential $E_e = -1.3$ V in the course of 60 s, after which the dissolution current of the resulting amalgam was recorded at a linear potential sweep at a rate of 60 mV s^{-1} . The interval of potential scanning was from -1.3 to 0.1 V. In the course of the experiment, reproducible analytical signals of the elements were recorded, and then a certain amount of ground glass was added and the solution was agitated for 5 min without recording any voltammograms. Then the agitation was terminated and the substances under study was again accumulated on the electrode. After reproducible voltammograms were recorded, a new portion of the adsorbent was introduced and the solution was again agitated for 5 min. The elements to be determined were accumulated and voltammograms were recorded from an unagitated solution, because recording with an agitated solution with an adsorbent yielded unsatisfactory results as a consequence of the irreproducibility of hydrodynamic conditions and adhesion of adsorbent particles to the electrode sur-

Table 1. Chemical composition of laboratory glass of various brands

Glass	Content, wt %							
	SiO ₂	B ₂ O ₃	Al ₂ O ₃	CaO	MgO	BaO	Na ₂ O	K ₂ O
Pyrex	80.64	12.0	2.0	0.36	–	–	4.0	1.0
MG	7.0	35.0	23.0	6.3	14.2	4.3	–	–
Glass no. 23	68.4	2.7	3.9	8.5	0.08	–	9.4	7.1

face. The extent to which the signal of the element being determined decreased was calculated by the formula

$$I_{\text{rel}} = \frac{\Delta I}{I} = \frac{I_0 - I_m}{I_0}, \quad (1)$$

where I_0 is the peak current measured without adsorbent addition, and I_m is the peak current in the presence of an adsorbent in an amount m (g).

The adsorption of ions was calculated by the equation

$$\Gamma = \frac{(c_{\text{in}} - c_{\text{f}})}{1000m}, \quad (2)$$

where Γ is the adsorption (mol g⁻¹); c_{in} , initial concentration of metal ions in the starting solution (M); c_{f} , concentration of metal ions in solution in the presence of an adsorbent (M); V , solution volume (ml); and m , mass of the adsorbent (g).

The pretreatment of the glass included several stages: (1) glass grinding in an agate mortar and sieving with a mesh of 1.5 mm; (2) boiling of the resulting powders in triple-distilled water, with water replaced several times to remove adsorbed contaminants; and (3) drying of filtered-off glass powder in an oven at 150°C.

Table 2. Current I of anodic peaks of heavy metal ions for various brands of glass. Supporting electrolyte 0.01 M KCl; $c_{\text{Cd}^{2+}} = c_{\text{Pb}^{2+}} = 4 \times 10^{-7}$, $c_{\text{Zn}^{2+}} = 9 \times 10^{-7}$ M; $E_e = -1.3$ V; $t_e = 60$ s; $V_s = 60$ mV s⁻¹

Glass	I , μA		
	Zn ²⁺	Cd ²⁺	Pb ²⁺
Pyrex	14.0 ± 1.0	13.0 ± 1.1	17.0 ± 1.5
MG	14.6 ± 1.2	19.8 ± 2.3	19.0 ± 2.0
ChG no. 23	9.2 ± 0.5	9.6 ± 0.6	10.6 ± 1.0

Molybdenum glass (MG), chemical glass no. 23 (ChG), and Pyrex were used in the study. Table 1 lists the chemical compositions of the glasses. Their chemical resistance decreases in the order Pyrex > MG > ChG. In the same order vary the heat resistance, brittleness, and hardness.

It should be noted that the magnitudes of the analytical signals of the elements to be determined and their relative values depended on the brand of a glass used to fabricate electrochemical cells (Table 2). The weakest signals were recorded in a cell made of ChG, and the strongest signals, in an MG cell. The greatest difference was observed for the signal of cadmium: The peak current decreased twice in going from MG to ChG. The results obtained indicate that the adsorption of heavy metal ions on the glass surface is strong and selective.

To determine the optimal time of agitation of a solution with the adsorbent, we measured the kinetic curves. These curves demonstrate that the analytical signal decreases as a result of adsorption of an element to be determined during the first 5 min. Upon further agitation, the signals of lead and cadmium remained virtually unchanged, and that of zinc changed only slightly. The efficiency of suppression of the analytical signal (anodic current peak) of the metal ions under study was analyzed as a function of the mass of the glass added. The scatter of experimental data in parallel measurements did not exceed 10%.

Figure 1 shows the dependences of the extent to which the peak currents I_{rel} of heavy metal ions simultaneously present in solution decrease on the mass of Pyrex glass added. The analytical signals of the elements under study were suppressed on introducing this brand of glass into solution when its mass increased to 0.20 g. The extent of depression of the signal was the greatest for Pb²⁺ ions and decreased in order Pb²⁺ > Zn²⁺ > Cd²⁺ (Fig. 1). A similar dependence was obtained with ChG. With MG used as adsorbent, the maximum depression of signals was observed even on introducing it into solution in an amount of 0.15 g. The extent to which the signal was

suppressed decreased in the order $Zn^{2+} > Pb^{2+} > Cd^{2+}$. It was established that the adsorption of the ions under study is the strongest on molybdenum glass and the weakest on Pyrex. The strongest difference was observed in the case of adsorption of Cd^{2+} ions. For example, the signal of cadmium decreased by 23% on introducing 0.24 g of powdered Pyrex and by 63% on introducing an MG powder of the same mass. The difference in the adsorbability of zinc and lead ions is considerably less pronounced. The peak current decreased, depending on the brand of glass, by 70–90% for Zn^{2+} and by 74–85% for Pb^{2+} . Thus, it was established that cadmium ions are adsorbed on the glass surface to the smallest extent, but the selectivity of their adsorption is the highest. Data on how the analytical signals of the elements under study decrease in the presence of powdered glass of various brands are presented in Fig. 2.

It should be noted that the adsorbability of the ions under study on glass powder differs from that on a flat surface. Table 2 shows that the adsorption of the ions is the weakest on the MG surface (peak currents are the highest), whereas the analytical signals of the ions are the lowest in the presence of a powdered glass of this brand, which indicates that their adsorption is the strongest. Possibly, grinding of MG gives rise to a greater number of active centers per unit surface, compared with other brands of glass. At the same time, grinding of different brands of glass may yield particles of unequal sizes because of the difference in hardness between these glasses, which affects the surface area of the adsorbent. This circumstance invites further analysis.

It is known that heavy metal ions are specifically adsorbed on solid surfaces [7]. However, competitive adsorption of Zn^{2+} , Pb^{2+} , and Cd^{2+} ions and indifferent cations of the supporting electrolyte, whose concentration is several orders of magnitude higher than that of heavy metal ions, must be observed in the presence of a large excess of a supporting electrolyte. Our experiments show that raising the concentration of the supporting electrolyte leads to a significant decrease in the adsorption of Zn^{2+} , Pb^{2+} , and Cd^{2+} ions. This is manifested in a decreased depression of the analytical signal. Table 3 illustrates the influence exerted by the concentration of the supporting electrolyte (KCl) on the degree of suppression of the peak current of heavy metal ions in the presence of powdered glass of various brands ($m_g = 0.1$ g). Table 3 shows that raising the concentration of the supporting electrolyte to 1 M minimizes the adsorption of the ions being determined. In this case, cadmium ions are virtually not adsorbed at all, and the

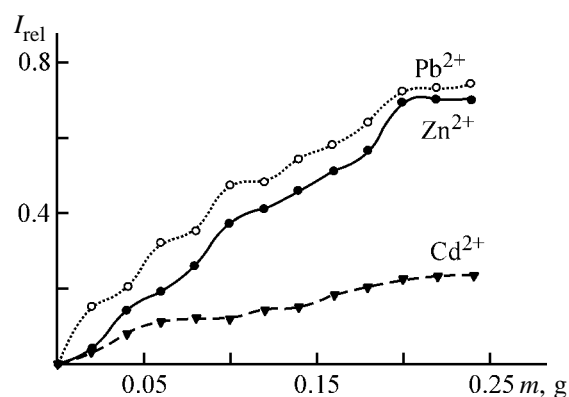


Fig. 1. Extent to which the currents of the anodic peaks of heavy metal ions are suppressed, I_{rel} , vs. the mass m of powdered Pyrex glass. Supporting electrolyte 0.01 M KCl; $c_{Cd^{2+}} = c_{Pb^{2+}} = 4 \times 10^{-7}$, $c_{Zn^{2+}} = 9 \times 10^{-7}$ M; $E_e = -1.3$ V; $t_e = 60$ s; $V_s = 60$ mV s $^{-1}$; the same for Fig. 2.

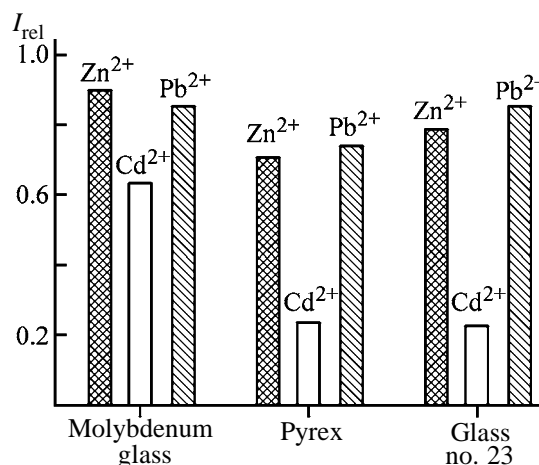


Fig. 2. Maximum extents of depression of the analytical signals I_{rel} of heavy metal ions in the presence of powdered glass of various brands ($m_g = 0.24$ g).

signals of zinc and lead are suppressed by less than 30%. Irrespective of the glass brand and concentration of the supporting electrolyte, the adsorbability of heavy metal ions decreases in order $Pb^{2+} > Zn^{2+} > Cd^{2+}$. Zn^{2+} ions are best adsorbed on the ChG surface, and Cd^{2+} ions, on the MG surface. The brand of a glass on whose surface Pb^{2+} ions are adsorbed to the greatest extent changes as the concentration of the supporting electrolyte increases.

The adsorption of ions also depends on the concentration of ions being adsorbed. On determining the concentrations of heavy metal ions before and after adsorption by the SVA method, their adsorption Γ on the surface of various brands of glass was calculated using Eq. (2). The results obtained with Zn^{2+} , Pb^{2+} , and Cd^{2+} at their concentrations in the range 10^{-7} – 10^{-5} M are given in Table 4. An increase in the concentration of the ions in solution shifts the adsorption–

Table 3. Depression of the current of anodic peaks of heavy metal ions in the presence of a powder of various brands of glass at different concentrations of the supporting electrolyte. $c_{\text{Cd}^{2+}} = c_{\text{Pb}^{2+}} = 4 \times 10^{-7}$, $c_{\text{Zn}^{2+}} = 9 \times 10^{-7}$ M; $E_e = -1.3$ V; $t_e = 60$ s; $V_s = 60$ mV s⁻¹; $m_g = 0.1$ g

c_{KCl} , mol g ⁻¹	$\Delta I/I_0$								
	Pyrex			MG			ChG no. 23		
	Zn ²⁺	Cd ²⁺	Pb ²⁺	Zn ²⁺	Cd ²⁺	Pb ²⁺	Zn ²⁺	Cd ²⁺	Pb ²⁺
0.001	0.35	0.14	0.45	0.38	0.32	0.63	0.53	0.33	0.70
0.01	0.29	0.12	0.42	0.35	0.27	0.52	0.35	0.16	0.49
0.1	0.20	0.09	0.35	0.27	0.13	0.42	0.26	0.09	0.27
1.0	0.14	0.05	0.26	0.17	0.09	0.30	0.21	0.04	0.15

Table 4. Adsorption Γ of heavy metal ions at their different concentrations in solution. Supporting electrolyte 0.01 M KCl, $T = 20^\circ\text{C}$

$c_{\text{M}^{2+}}$, mol g ⁻¹	$\Gamma \times 10^8$, mol g ⁻¹								
	Pyrex			MG			ChG no. 23		
	Zn ²⁺	Cd ²⁺	Pb ²⁺	Zn ²⁺	Cd ²⁺	Pb ²⁺	Zn ²⁺	Cd ²⁺	Pb ²⁺
10 ⁻⁷	1.5	0.48	0.70	1.7	0.69	0.79	1.9	0.46	0.78
10 ⁻⁶	3.0	1.2	1.1	3.0	1.3	1.3	2.9	1.1	1.3
10 ⁻⁵	14	10	–	17	10	–	14	10	–

desorption equilibrium toward the adsorption process. If the concentration of the ions being adsorbed increases by an order of magnitude, their adsorption becomes 1.5–2 times stronger. At a concentration of the ions in solution on the order of 10⁻⁵ M, the analytical signals of lead and cadmium are overlapped, which hinders their identification. Therefore, the adsorption of zinc and cadmium ions at their content in solution of 1 × 10⁻⁵ M was determined in the absence of lead ions. In this case, the amounts of adsorbed Zn²⁺ and Cd²⁺ ions became closer to each other. The data obtained suggest that the adsorption of heavy metal ions is competitive: adsorption of Pb²⁺ ions hinders adsorption of Cd²⁺ ions. In the absence of lead ions, the adsorption of cadmium ions is considerably stronger.

The study performed demonstrated the importance of adsorption processes at the glass–solution interface in determining low concentrations of ions, which may make incorrect the analytical results. The adsorption of heavy metal ions can be markedly diminished by an appropriate choice of the material of a storage vessel and electrochemical cell and also by use of sufficiently concentrated supporting-electrolyte solutions. To make smaller the determination error, it is recommended to prepare reference solutions in a supporting electrolyte rather than in pure water.

REFERENCES

1. Korenman, I.M., *Analiticheskaya khimiya malykh kontsentratsii* (Analytical Chemistry of Low Concentrations), Moscow: Khimiya, 1966.
2. Voskresenskii, P.I., *Tekhnika laboratornykh rabot* (Manual of Laboratory Works), Leningrad: Khimiya, 1970.
3. Fridrikhsberg, D.A., *Kurs kolloidnoi khimii* (A Course of Colloid Chemistry), Leningrad: Khimiya, 1974.
4. Bond, A.M., *Polyarograficheskie metody v analiticheskoi khimii* (Polarographic Methods in Analytical Chemistry), Moscow: Khimiya, 1983.
5. Brainina, Kh.Z., Neiman, E.Ya., and Slepshkin, V.V., *Inverzionnye vol'tamperometrichekie metody* (Stripping Voltammetric Methods), Moscow: Khimiya, 1988.
6. Vydra, F., Štulík, K., and Juláková, E., *Rozpouštěcí polarografie a voltametrie*, Prague: Nakl. Technické Literatury, 1977.
7. *Adsorption from Solution at the Solid/Liquid Interface*, Parfitt, G.D. and Rochester, C.H., Eds., London: Academic, 1983.
8. Zakharova, E.A. and Pikula, N.P., *Inverzionnaya vol'tamperometriya* (Stripping Voltammetry), Tomsk: Tomsk. Gos. Univ., 1995, p. 35.