

ANALYSIS OF STANDARD SAMPLES BY THE INVERSE VOLT-AMPEROMETRY METHOD OF SOLID PHASES. DETERMINING SILVER IN LEAD

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The inverse volt-amperometric method of solid phases is well known in native literature as the method of film polarography with an accumulation or film volt-amperometry. The source of the information in this method is contained in the polarization curves of the electrochemical transformation of metal or of a chemical compound.

The term, which is extended in the title of the given article, obviously more accurately reflects the essence of the method, since an electroactive solid phase does not always form a film on an electrode surface and the process is the "reverse" as compared with a solution. Even in the case where a so-called "film" electrode is used, when mercury is isolated with the determined metal, a film is not always formed, since the solubility of metals in mercury sometimes is lower than the actual concentration on the electrode.

A number of versions of this method, which we shall call inverse volt-amperometry of metals (IVM), of ions of variable valence (IVI), and of anions (IVA), is known [1].

We used the method of inverse volt-amperometry of solid phases for analyzing standard samples and spectral standards of nonferrous and ferrous metals and alloys. On the basis of statistical data, the sensitivity of the determinations and the reproducibility of the results were objectively determined.

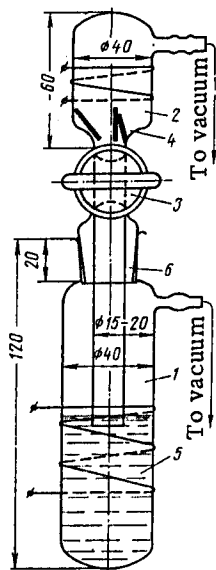


Fig. 1. Device for impregnating graphite electrodes: 1) the thick-walled test tube; 2) the vessel for degassing the electrodes; 3) the vacuum valve; 4) graphite bars; 5) ED-6 resin; and 6) the directing tube.

The use of the IVM method for determining micro-quantities of silver in lead is effective in connection with the fact that the great difference of potentials of the Ag^+/Ag and Pb^{2+}/Pb systems permits making an analysis without a preliminary separation of the element, and the complications which develop when using a mercury electrode, whose oxidation current generally masks the discharge-ionization currents of silver, are eliminated.

The authors of a number of articles concentrate silver on vitreous graphite [2]; on a graphite electrode impregnated with wax [3]; on a platinum electrode [4]; and on a graphite electrode impregnated with an epoxide resin with polyethylene polyamine [5]. The indicated sensitivity of the determinations varies from $1 \cdot 10^{-5}$ to $1 \cdot 10^{-7}\%$. An objective evaluation of the greatest possible sensitivity of determining silver is not brought out in the articles.

As an indicator, we used the most investigated graphite electrode, impregnated with an epoxide resin with polyethylene polyamine.

The electrode was prepared in the following manner. To 10-15 g of heated ED-6 resin an equal volume of acetone was added and mixed, and 0.2 ml of polyethylene polyamine was introduced. The

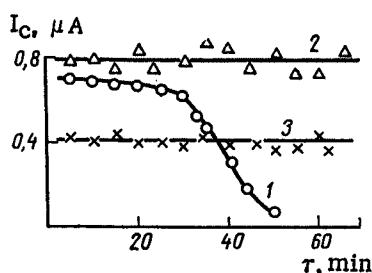


Fig. 2

Fig. 2. The effect of the method of preparing an electrode surface on reproducing the results of determining silver. The electrolyte volume was 20 ml, the duration of accumulation was 3 min, 0.5 μ g Ag, and 0.2 g Pb, and the scanning speed potential was 1 V/min; 1) electrochemical refining with polarization at +0.2 V; 2) mechanical refining after each measurement; and 3) polarization with a potential of +0.02 V, 2 min in a solution consisting of 0.2 μ g Hg (11).

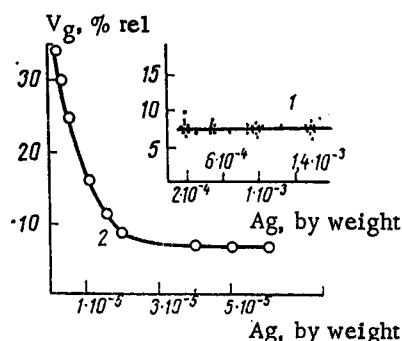


Fig. 3

Fig. 3. The dependence of the variation factor on silver concentration: 1) $5 \cdot 10^{-7}$ – $5 \cdot 10^{-6}$ M ($1 \cdot 10^{-4}$ – $2 \cdot 10^{-3}$ ‰); and 2) $2 \cdot 10^{-10}$ – $4 \cdot 10^{-8}$ M ($5 \cdot 10^{-7}$ – $6 \cdot 10^{-5}$ ‰).

TABLE 1. Determining Silver in Lead Standards by the IVM Method

Silver content, ‰ by weight	Variation factor, ‰ rel. to v	Silver content, ‰ by weight	Variation factor, ‰ rel. to v
0.00022	7.18	0.00092	8.05
0.000205	7.44	0.00117	8.96
0.00025	6.87	0.00102	6.61
0.00024	9.23	0.00109	6.55
0.00028	7.01	0.00101	7.46
0.00023	8.00	0.00092	7.63
0.00044	7.14	0.00154	5.60
0.00048	6.29	0.00188	7.57
0.00051	8.23	0.00203	11.23
0.00047	8.53	0.00186	7.54
0.00049	7.25	0.00179	8.14
0.00053	7.31		

mixture was heated for removing the acetone and was transferred to a thick-walled test tube equipped in the upper part with a ground-glass joint. Rods cut from spectral graphite with a diameter of 2 mm and a length of 10–15 mm were placed in a vessel furnished with a vacuum valve with a wide transfer aperture of 15–20 mm, and with a ground-glass joint. The test tube and the vessel have a winding for heating. The temperature was regulated by using a transformer.

Both parts of the apparatus (Fig. 1) were connected, and the air was pumped out for 30–50 min at a temperature sufficient for keeping the mixture in a liquid state, and then the rods were saturated in resin in a vacuum for 6 h. The bars were removed and were left in the atmosphere until the resin was completely hardened. The heat treatment was conducted at 100–200°C for 6 h.

The ends of the bars were cut, and each of the bars was inserted in the glass tube, heated and immersed in polyethylene powder, and fused. This operation was repeated four to five times. Electrical contact was made through mercury or a carbon powder.

The electrodes prepared in the described manner operate for several months. It should be noted that, in developing the method of preparing the electrodes, we did not raise the problem of comparing the advantages of this or that type of graphite element, but we aimed for a unifying impregnation method so that the results obtained by the various investigators could be compared.

As a background, solutions comprising 0.01–0.1-M KSCN were used [2, 6]. In the more concentrated solutions of potassium rhodanide, lead rhodanide, which coprecipitates silver ions, is crystallized. In order to avoid forming a sediment, small batches of lead were used. The experiment was carried out at 35–40°C.

Extremely pure nitric acid, doubly distilled in a quartz apparatus, was used. The potassium rhodanide solutions were prepared from analytical grade, twice-crystallized compound.

The solution was deaerated and mixed using a flow of spectrally pure argon. The 7-77-4/B (Hungary) and the PO-5122 Central Laboratory of Automation polarographs were used.

The results obtained with different methods of preparing the electrode are compared in Fig. 2. The conditions are clear from the caption under the figure. Electrochemical refining (curve 1) ensures reproducibility of the maximum current within the limits of 3-5% for 15-20 min. The maximum current was quickly decreased, apparently as a result of adsorption of surface active materials.

With the mechanical restoration of the electrode surface (curve 2) the reproducibility of the results in time is improved, but the relative error increases to 12-15%. The introduction of mercury (11) into the examined solution in a quantity equal to the content of silver (curve 3) ensures the reproducibility of the values of the maximum current with a relative error of 3-5%. However, with the latter, the hazard of the influence of the current of the mercury solution on the anode current of silver arises; therefore, subsequently we combined electrochemical refinement with mechanical restoration of the electrode surface after each fourth measurement.

The dependence of the magnitude of the maximum current of an electrosolution of silver on metal ion concentration in a solution is directly proportional in nature.

0.1-0.2 g of lead were dissolved in 10 ml of HNO_3 (1:1), the solution was evaporated until dry, and the residue was dissolved in 15-20 ml and 0.05-M KSCN with a slight heating and was transferred to a thermostated electrolyzer and deaerated 7-10 min with an argon current. The silver was previously concentrated on a graphite electrode with a potential of -0.4 V (sat. cal. el.) for 5-10 min. The mixings were discontinued and the solution was allowed to settle for 30 sec, and the anode volt-ampere curve was recorded for the linearly changing potential in time. The maximum current of the silver solution was observed to be -0.05 V.

Table 1 shows the results of determining silver in spectral standards of high-purity lead.

The value of the variation factor amounted to 7-8% over wide limits of silver concentration (Fig. 3, curve 1). The latter verifies the fact that determining silver by the IVM method can be accomplished with considerably higher sensitivity.

For an objective evaluation of the sensitivity of determining silver by the IVM method, we examined the change of the variation factor in the $2 \cdot 10^{-10}$ - $2 \cdot 10^{-6}$ M ($5 \cdot 10^{-7}$ - $5 \cdot 10^{-3}\%$) (curve 2) concentration range. The results were calculated on an ÉSM "Dnepr."

The distribution of the variation factor with concentration shows that the actually attained sensitivity of determining silver by the IVM method is close to $1 \cdot 10^{-9}$ M according to the trisigmoid criterion with a 15 min duration of concentration, which with a batch of 0.1 g represents $2 \cdot 10^{-6}\%$. In evaluating sensitivity, the extent of the idle experiment was not calculated since the current of the idle experiment equalled zero.

Lesser concentrations can be determined with an error significantly greater than the indicated amount.

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