Chemistry

S. I. Sinyakova and Shen Yu-Chi

1960

SovietRxiv

Abstract

Full Text

Chemistry

S. I. Sinyakova and Shen Yu-Chi

Determination of Ultramicro Quantities of Metals Using a Polarograph and a Stationary Mercury Drop as Electrode

(Presented by Academician A. P. Vinogradov on 2 September 1959)

In connection with the need to improve the polarographic method of analysis in the direction of increasing its sensitivity, a new branch of it has arisen—oscillographic polarography—which makes it possible to increase the sensitivity of the method by 1-2 orders of magnitude. However, when an ordinary polarograph is used, the possibilities for increasing sensitivity have likewise not yet been exhausted. Promising in this respect is the use of catalytic currents (^1), as well as new electrodes (rotating dropping mercury (^2), stationary mercury (^3), and various solid ones (^4)). The highest sensitivity can be achieved by using stationary spherical mercury electrodes of small surface area, if electrolysis is first carried out at a constant potential to deposit ions into the mercury with formation of amalgams (for concentrating the elements), and then the metals are dissolved anodically, using an ordinary polarograph to record the curves. Most works in which a stationary electrode in the form of a "hanging" or "resting" drop was used were performed with an oscillographic polarograph. Kemula and Kublik (^5) used for this purpose an ordinary polarograph and an electrode in the form of a "hanging" mercury drop, and showed that impurities of certain metals in reagents can be detected at concentrations down to 10^{-8} M. However, these authors do not present systematic quantitative studies.

In the present article it is shown that, by applying preliminary enrichment on a stationary mercury drop, it is possible to carry out quantitative determination of a number of elements that form amalgams with mercury (Cu, Cd, In, Pb, Zn, etc.) from anodic-dissolution curves at their concentration in solution down to 10^{-8} M. To establish the optimum conditions for conducting the analysis, the influence of various factors (drop surface size, duration of electrolysis for enrichment, rate of stirring of the solution, temperature, etc.) on the magnitude of the anodic-dissolution currents of the metals was systematically studied. A modified Nickelli–Kuka cell (^6), shown in Fig. 1, was used. The main electrode in the cell was a "resting"mercury drop on a capillary, its formation being effected by a definite number of turns of a stopcock. The capillary was preliminarily coated with a film of chlorosilane. The other electrode was a saturated calomel electrode, the end of which was lowered into the solution near the mercury drop.

Stirring of the solution during the preliminary electrolysis was carried out by a stream of nitrogen blown through at a controlled rate.

Into the electrolyzer were placed 20-40 ml of previously carefully purified electrolyte (0.2 M KCl, KNO_3, HCl); such a volume of solution containing the ion under investigation was added that its final concentration was 10^{-6}-10^{-8} M; then the nitrogen stream was turned on to stir the solution, estab-

the rheostat slider to a voltage 0.2-0.3 V more negative than the half-wave potential of the ion being determined, and connected both electrodes to the polarograph while simultaneously starting the stopwatch. Electrolysis was carried out for a fixed time (10-30 min), with the nitrogen stream switched off one minute before its completion (the mercury drop came to rest). After electrolysis was completed, the curve of anodic dissolution of the metal from the amalgam was recorded, running the polarograph in the reverse direction, i.e., from more negative to more positive potential values. In this way curves of anodic dissolution of metals were obtained, shown in Fig. 2. The position of the minimum current of these curves on the potential axis characterizes the nature of the element, while its magnitude is determined by the concentration of the metal in the amalgam. The graphical method we used for measuring the minimum currents is also shown in the same figure.

Fig. 1. Electrolyzer. **1** –electrode with a "resting" drop; **2** –saturated calomel electrode; **3** –nitrogen inlet

Using the determination of a very dilute lead solution (0.1 γ/ml) as an example, it was established that the surface area of the mercury drop (Fig. 3), the rate of stirring of the solution, the duration of electrolysis, and the temperature have a large influence on the magnitude of the minimum current of lead. However, if these conditions are kept constant, well-reproducible results can be obtained. The most optimal conditions for the analysis, as our experiments showed, are: drop diameter 1.3-1.6 mm, rate of stirring of the solution not less than 80 mm water column,* electrolysis time 10-30 min. Raising the temperature increases the sensitivity of the method. (The temperature coefficient of the current is equal to 3% in the temperature range 20-60°.) Under standard experimental conditions, a rectilinear dependence of the magnitude of the minimum current on concentration was obtained for a number of elements (Pb, Cu, In, Zn) in the concentration range 10^{-7}-10^{-8} M (Fig. 4), which indicates the reliability of the proposed analytical method.

Fig. 2. Curve of anodic dissolution of metals from amalgam. Concentrations: Zn 0.01 γ/ml ($1.6 \cdot 10^{-7}$ M), In 0.005 γ/ml ($4.5 \cdot 10^{-8}$ M), Pb 0.01 γ/ml ($5 \cdot 10^{-8}$ M), Cu 0.01 γ/ml ($1.7 \cdot 10^{-7}$ M)

Fig. 3. Dependence of the minimum current of anodic dissolution of lead on the size of the surface of the mercury drop ($C_{\text{Pb}} = 0.1$ γ/ml). **1** –with a capillary coated with a chlorosilane film; **2** –with an uncoated capillary

The magnitude of the minimum current is determined by two processes: the

Fig. 4. Dependence of the magnitude of the anodic dissolution current of metals on the concentration of their ions in solution

Figure 1: Fig. 4. Dependence of the magnitude of the anodic dissolution current of metals on the concentration of their ions in solution

rate of deposition of metal ions on the stationary mercury cathode and the rate of

* Internal diameter of the tube 3.5 mm.

anodic dissolution of the metal from the amalgam. The first process depends on the rate of convective diffusion of ions to the surface of the drop, and the theory of the diffusion layer is applicable to it. It can be described by the equation

$$C = C_0 e^{-\frac{ADt}{VS}}, \tag{1}$$

where C_0 is the initial concentration of ions (g-ion/ml); C is the concentration of ions at time t (sec.) from the volume V (ml) and from the cathode surface equal to A (cm^2); D is the diffusion coefficient (cm$^2 \cdot$ sec^{-1}); S is the thickness of the diffusion layer (cm).

Equation (1) can also be represented in the form

$$t = \frac{2.303VS}{AD} \log \frac{C_0}{C} = \frac{2.303VS}{AD} \log \frac{I_0}{I}. \tag{2}$$

Equation (2) makes it possible to calculate the time required for complete quantitative deposition of metals in mercury. However, in contrast to the method of Hickling et al. (^{7}), who used a stationary mercury electrode of large surface area (1 cm^2) and quantitative deposition of metals in mercury, the method we propose for concentrating elements in the amalgam does not require their quantitative deposition. It is only necessary that, with the stirring rate and other conditions kept constant, the amount of the element deposited be a linear function of its concentration in the solution at an unchanged duration of electrolysis, and a linear function of the duration of electrolysis at a constant concentration of the element. This dependence, as is evident from the results we obtained (Fig. 4), is observed quite satisfactorily.

Fig. 4. Dependence of the magnitude of the anodic dissolution current of metals on the concentration of their ions in solution

The second process—the anodic dissolution of the metal—is determined mainly by the rate of diffusion of the metal in mercury to the amalgam–electrolyte interface, as well as by the magnitude of the amalgam surface, temperature, and other factors (^{8}). The values we obtained for the anodic dissolution currents of lead, cadmium, indium, and zinc correlate well with the values of the diffusion coefficients of these metals in mercury (^{9}), and also with their solubility in mercury (^{10}). The very low value of the anodic dissolution currents of copper cannot be explained solely by the lower value of its diffusion coefficient in mercury ($D =\sim 1.0 \cdot 10^{-5}$ cm$^2 \cdot$ sec^{-1}) and its low solubility in mercury (0.003%); apparently, copper forms a series of compounds with mercury which, according to Russell et al. (^{11}), may have compositions from Cu_7Hg to $CuHg_4$. In addition, the possibility of formation of intermetallic compounds during the dissolution of two or more metals in mercury cannot be excluded. However, these phenomena do not affect the quantitative determination of the indicated metals, apart from the reduced sensitivity of the method for copper. The presence in the solution of surface-active substances (gelatin and others) has a noticeable effect on the magnitude of the current, decreasing it. For example, the minimum current of lead decreases by 16% when the solution contains $1 \cdot 10^{-3}$% gelatin.

An important advantage of the proposed method is the possibility of determining several elements in one solution, since the magnitude of

neither elements dissolving from the amalgam at more negative potentials, nor those dissolving at more positive potentials (even when their content is tenfold or more relative to the element being determined) have any effect on the minimum current. This circumstance makes the method we propose quite suitable for the quantitative determination of several impurities simultaneously, whereas according to (7), only one metal can be quantitatively determined from anodic dissolution curves, since only the first metal dissolving from the amalgam gives the correct value of the limiting current, while the subsequent metals, dissolving at more positive potentials, give excessive currents, in the opinion of the authors of the method, as a result of an electrochemical displacement reaction.

Our studies also showed that repeated determination of ions can be carried out from one and the same solution, provided that the mercury drop is renewed each time. This makes it possible to use the method of additions for quantitative determinations of elements. Another important advantage of the method is the possibility of determining very low impurity contents in the presence in solution of a large excess of ions with a more negative reduction potential (for example, indium 0.05 γ/ml at an In : Co ratio $= 1 : 10^5$). For this purpose, enrichment of indium should be carried out by electrolysis at a potential more positive than the reduction potential of cobalt (at -0.9 V relative to the N.C.E.). The resulting value of the minimum current of anodic dissolution of indium is equal to its value in the absence of cobalt. The average relative error of the proposed method for element concentrations of 10^{-7}–10^{-8} M does not exceed \$±\$6%. The maximum deviations reach \$±\$15%.

The authors express their gratitude to Corresponding Member of the Academy of Sciences of the USSR I. P. Alimarin for valuable advice during the conduct of this work.

Institute of Geochemistry and Analytical Chemistry
named after V. I. Vernadsky

Received

24 VIII 1959

CITED LITERATURE

1. S. I. Sinyakova, M. I. Glinkina, *Zhurn. anal. khim.*, **11**, 544 (1956); Proceedings of the 4th Conference on Electrochemistry, 1959, p. 201.

2. W. Stricks, I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 2085 (1956); I. M. Kolthoff et al., *Anal. Chim. Acta*, **18**, 83, 295 (1958); N. Tanaka et al., *Anal. Chim. Acta*, **18**, 97 (1958).

3. C. Streuli, W. Cooke, *Anal. Chem.*, **25**, 1691 (1953); D. Rossie, W. Cooke, *Anal. Chem.*, **27**, 1360 (1955); R. Kalvoda, *Zav. lab.*, **24**, 1319 (1958).

4. S. I. Sinyakova, *Khimicheskaya nauka i promyshlennost'* , **4**, No. 2, 197 (1959).

5. W. Kemula, Z. Kublik, *Anal. Chim. Acta*, **18**, 104 (1958); *Roczn. Chem.*, **30**, 1005 (1956); **32**, 941 (1958).

6. J. G. Nikelly, W. D. Cooke, *Anal. Chem.*, **29**, 933 (1957).

7. A. Hickling, J. Maxwell, J. V. Shennan, *Anal. Chim. Acta*, **14**, 287 (1956).

8. A. Hickling, J. Maxwell, *Trans. Farad. Soc.*, **51**, 44 (1955).

9. W. C. Cooper, N. H. Furman, *J. Am. Chem. Soc.*, **74**, 6183 (1952).

10. A. G. Stromberg, A. A. Pushkina, Proceedings of the Commission on Analytical Chemistry, **7** (10), 136 (1956).

11. A. S. Russel, P. V. F. Cazalet, N. M. Irvin, *J. Chem. Soc.*, **1932**, 841, 852.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.