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VECTOR POLAROGRAPH EMPLOYING A STATIONARY DROP

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A study has been made of the performance of this instrument. The sensitivity and resolution have been determined as functions of the initial potential, sweep rate, time of preliminary electrolysis, and so on.

The dropping mercury electrode so widely used in polarography has some disadvantages that bar the way to improved sensitivity and resolution, namely capacity current and capillary noise. Current instruments provide limits of detection of 10^{-7} to 10^{-8} mole/liter and resolving powers of several thousand, but these do not satisfy all requirements in the metallurgy of high-purity metals or the production of rare elements, semiconductors, and so on. For this reason the stationary drop has attracted considerable attention; the main distinctive features of this are that the continuously changing surface and short reaction times (a few seconds) are replaced by a surface independent of time and a reaction time of hundreds or even thousands of seconds. The fixed surface eliminates the restriction on resolution inherent in the dropping electrode; moreover, a concentrated amalgam can be produced by prolonged preliminary electrolysis for many metals.

Barker [1-3] first used the stationary electrode to increase the sensitivity in ac (square-wave) polarography.

Here we describe some experiments performed on a vector polarograph designed here, which has a special system for producing the drop.

In vector polarography the polarizing voltage is accompanied by a sinusoidal voltage of small amplitude, which is taken from a source of low internal impedance.

The current through the cell can be represented as the sum of several components if the cell contains an indifferent electrolyte of high conductivity having one species of potential-determining ion that can be oxidized or reduced at the polarizable electrode. These include three sinusoidal components all having the frequency of the supply: the resistive and reactive components of the electrolytic current (from electrochemical reactions at the polarizable electrode) and the reactive component from the capacitance of the double layer at the interface. These three components are measured and used in the vector polarograph.

The required information may be derived from the individual components or from combinations of these (but not from the sum). Only one of the components of the electrolytic current is used for purely analytical purposes (identification and assay of solutes); the capacitance current merely represents an inconvenience.

The other reactive component has the same phase as the capacitance current, so it can be used in analysis only at fairly high concentrations. It is therefore usual to employ the resistive vector-polarogram, which is the resistive component as a function of polarizing voltage.

The vector-polarogram has a symmetrical bell shape (pronounced peak) for polarographically reversible electrode reactions; the height of the peak defines the concentration, while the position defines the nature of the component.

Two distinctive features of vector polarography with a dropping electrode are as follows:

1. The shape and height of the polarogram are not dependent on the law followed by the polarizing voltage; the electrode is given various fixed potentials, and the current is measured for each, all points being plotted on a single curve. The alternating current is governed only by the present value of the polarizing voltage for a given concentration and for a given frequency and amplitude of the alternating voltage.

2. The height of the vector polarogram is proportional to n^2 (square of number of electrons) and is independent of the charge on the products from the electrode reaction.

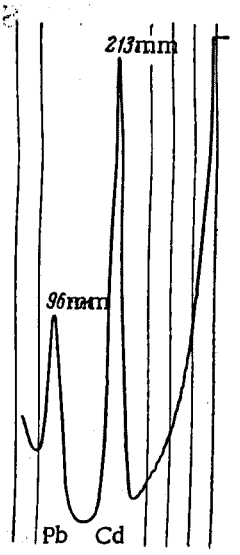

Fig. 1.

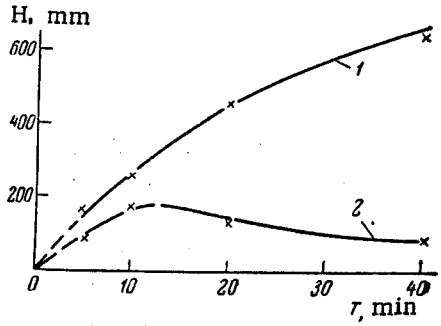

Fig. 2.

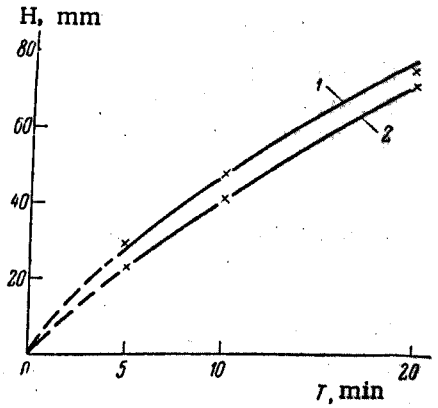

Fig. 3.

Fig. 1. Vector polarogram of lead and cadmium against N HCl as background; lead concentration 10^{-8} mole/liter, cadmium $2 \cdot 10^{-8}$ mole/liter.

Fig. 2. Wave height as a function of accumulation time in N HCl for 1) lead and 2) cadmium (concentrations 10^{-6} mole/liter).

Fig. 3. Wave height as a function of accumulation time in N HCl for 1) cadmium and 2) lead (concentrations 10^{-8} mole/liter).

The stationary-drop method also employs dc with ac; here the polarogram is recorded, but the current is here somewhat dependent on the rate of change of the polarizing voltage, so this is kept under strict control.

The law followed by the polarizing voltage may be formulated as follows:

$$E = E_i \pm (t - T)\frac{dE}{dt} \text{ for } t \geqslant T$$

and

$$E = E_i = \text{const for } t \leqslant T.$$

The electrode potential E is kept at a fixed value E_i for a time T; the electrolytic current is not measured during this time. From time t = T the potential is altered at a rate v = dE/dt, the automatic recording of the current starting from this moment. The sign in front of the bracket indicates the sense of change; anodic polarization (+) means the potential of the polarizable electrode becoming positive; cathodic (−), negative.

All the parameters (E_i, T, and v) affect the result when the electrode is stationary, as do the charge on the products and the hydrodynamic state of the solution in the period T (static or forcibly stirred).

The most characteristic conditions are as follows. The cell contains an indifferent electrolyte with only one species of potential-determining ion capable of being reduced to form an amalgam at the electrode, which is given a potential E_i more negative than the potential corresponding to the peak. The solution is stirred thoroughly for a time T, which gives at the electrode an amalgam whose concentration increases with time; the solution simultaneously becomes depleted. The volume of the solution is usually much greater than that of the drop, so the depletion of the solution can be neglected, and the concentration of the amalgam can therefore become high (hundreds or thousands of times that in the solution). The stirring is stopped at time T and the positive-going sweep is turned on.

The height of the wave is governed by the concentration in the amalgam, which is far higher than that in the solution; other things being equal, the two concentrations are uniquely related, so the initial concentration of the solution can be deduced from a suitable calibration. This is essentially the source of the increased sensitivity.

TABLE 1. Wave Height as a Function of Time for Cathode Polarization

τ, min	Height, mm	
	Pb	Cd
0	139	78
3	130	27
6	122	20

TABLE 2. Peak Heights H_a and H_r for Resistive and Reactive Polarograms as Functions of T*

τ, min	Lead			Cadmium		
	H_a (mm)	H_r (mm)	$H_r:H_a$	H_a (mm)	H_r (mm)	$H_r:H_a$
3	51	50	0.98	59	34	0.58
6	95	88	0.93	87	44	0.51
9	103	83	0.80	54	22	0.41
18	146	61	0.42	24	7	0.29

* H_a and H_r were recorded at different sensitivities.

Figure 1 illustrates this by reference to the curve for 10^{-8} mole/liter Pb + 2×10^{-8} mole liter Cd against N HCl as background ($E_i = -1.1$ V, T = 10 min, v = mV/sec, $\Delta E_\sim = 4$ mV, sensitivity 1).

Tests have shown that the reproducibility for lead is entirely satisfactory, but the spread for cadmium is much greater (the maximum deviation of the wave height was 20 mm). The reasons for this are considered below.

The lead was an impurity that could not be removed from the background, so lower concentrations of lead could not be determined directly, although concentrations below 10^{-9} mole/liter are clearly accessible. For comparison, the limit for a dropping electrode under analogous conditions is $\geq 10^{-7}$ mole/liter.

The amount of material deposited is proportional to the time for which the current was passed, so we may suppose that the height H is proportional to T. This was tested by recording a series of the above curves with all conditions (apart from the time) constant: 10^{-6} mole/liter Pb + 10^{-6} mole/liter Cd, background N HCl, $E_i = -1.1$ V, v = 6 mV/sec, $\Delta E_\sim = 4$ mV, sensitivity 1/16.

The H-T graphs of Fig. 2 were thereby constructed, which show that the wave height for lead increases with T, but not linearly; whereas cadmium shows a rise for T small, with later a maximum*.

This anomalous behavior is to be ascribed to surface-active impurities present in the background, for the surface of the drop accumulates these, which causes the rate-constant to become a function of time. The resulting change can be very large. Previously reversible electrode reactions may become partly or completely reversible under these conditions; the wave height is then reduced.

The wave height is then a function of two time-dependent factors (concentration and rate-constant), other conditions being unchanged. The concentration increases with T, but the rate-constant decreases; the first factor is dominant at first, so the wave height increases, but the second becomes dominant as T increases, so the height falls.

Figure 3 shows H-T curves for lead and cadmium (10^{-8} mole/liter) in especially purified HCl ($E_i = -1.1$ V, $\Delta E_\sim = 4$ mV, v = 4 mV/sec, sensitivity 1/2); lead and cadmium behave identically in this case.

The effects of surface-active materials may be examined by deliberately introducing these; but then it is difficult to use anode polarization, for high negative polarization and high concentrations of surface-active materials cause either spontaneous breakaway or interruption of the contact in the capillary, although the drop remains hanging.

The effects have been tested in cathode polarization with lead and cadmium (10^{-4} mole/liter) in N HCl containing three drops of 1% glue solution in 25 ml. The initial potential was −0.2 V. Only adsorption of the surface-active materials occurred in this case (Table 1); no amalgam was formed.

It is clear from this that surface-active materials influence the wave height.

There are several tests that establish that these materials act via the rate-constant; some apply to ac polarography generally and some only to vector polarography. The first is the effect on the position and half-width of the peak (the latter increases); but this is difficult to use, for appreciable effects occur only for changes in rate-constant of several orders of magnitude.

* The H-T curve for lead also shows a peak under some conditions.

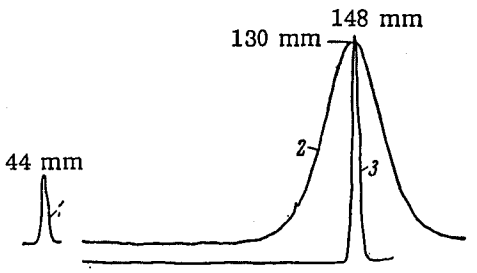

Fig. 4.

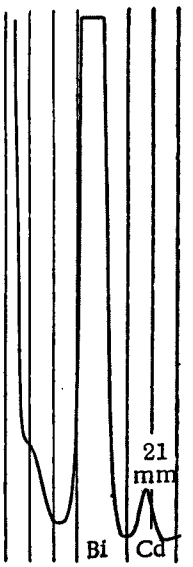

Fig. 5.

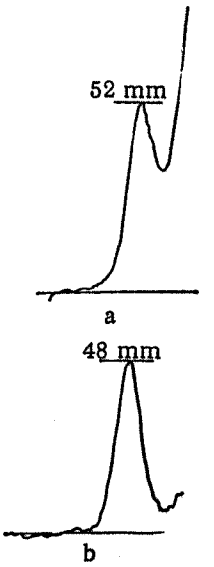

Fig. 6.

Fig. 4. Vector polarograms of lead (10 g/liter) against N HCl recorded at different sweep rates: 1-3 represent rates of 9.8, 1.0, and 9.8 mV/sec respectively.

Fig. 5. Vector polarogram from cadmium in the presence of bismuth in hydrochloric acid.

Fig. 6. Polarograms of: a) 0.1 mg/liter Cd + 2000 mg/liter Cu and b) 0.1 mg/liter Cd, with ammonia background.

A test specific to vector polarography is the ratio between the resistive and reactive components. The equivalent circuit of the TsLA vector polarograph is that of a capacitance in parallel with a resistance; the resistive and reactive components are equal for reversible reactions, and $K_G > 0.15\sqrt{2\pi f}$; K_G is the rate constant and f is frequency in c/s ($K_G > 2.67$ cm/sec for 50 c/s) [5].

The reaction becomes partly or completely irreversible as K_G falls; both components fall for partly reversible reactions, but the fall in the reactive one is large, so the phase shift is reduced. An irreversible reaction with change of K_G causes merely a shift in the peak to the negative side without effect on the components; the phase shift is then independent of the rate constant.

This means that additional evidence on the electrode processes can be obtained from comparison of the resistive and reactive polarograms. Table 2 lists ones we have recorded in this way with unpurified N HCl, $2 \cdot 10^{-6}$ mole/liter Cd, 10^{-6} mole/liter Pb, $E_i = -0.9$ V, $E = 4$ mV, and $v = 6$ mV/sec.

H_r/H_a decreases as T increases, so the rate constant must fall. The H-T curves for lead are of interest; the resistive one rises monotonically, whereas the reactive one has a peak.

Ac polarography generally allows one to measure the current associated with the capacitance of the double layer throughout T. Adsorption of surface-active material causes this to vary with time, but the capacitance and electrolytic currents follow different and unrelated laws. We have encountered cases in which the capacitance current had varied by a factor 2 at T = 30 min whereas the rate constant had varied by about a factor 100,000 and the useful signal by about a factor 12.

The wave height is not linearly related to electrolysis time, but this does not interfere with the use of the method, provided that constant conditions are maintained for unknown and standard. Accidental impurities may greatly reduce the accuracy and reproducibility; addition of a substantial amount of surface-active material improves the accuracy, but a stable hanging drop may then be unobtainable. This means that very careful purification of background and mercury is needed if the concentrations to be measured are very low*.

We now consider some conditions of practical importance to establish the effects of sweep rate on peak height.

* The stopcocks should not be lubricated with organic materials, in order to prevent contamination; they operate quite satisfactorily if lubricated with chemically pure graphite.

TABLE 3. Wave Height for Molybdenum as a Function of Sweep Rate

Rate, mV/sec	1.00	4.15	9.8	16.5
Height, mm	60	59	61	65
	63	61	62	70
	—	60	66	66

TABLE 4. Wave Height for Thallium as a Function of Initial Potential and Accumulation Time

E_i, V	Height, mm, for time of		
	5 min	10 min	20 min
−0.8	61	83	63
−1.1	69	106	135

Condition I. Reduction gives an amalgam; the preliminary electrolysis is performed with stirring, and anodic polarization is used.

Sweep rates of 1.00, 4.15, 9.8, and 16.5 mV/sec were used with 0.1 mg/liter of Cd on ammonia as background ($E_i = -1.2$ V, $\Delta E_\sim = 4$ mV, T = 6 min, sensitivity 1/32); these gave the following mean peak heights (three measurements each): 67, 83, 90, and 85 mm.

The sweep rate therefore has little effect on the peak height in anodic polarization; the slight fall at the lowest speed is associated with depletion of the surface layer consequent on diffusion of the metal into the drop. The best approach is therefore to use the maximum rate compatible with the response time.

Condition II. The component is reduced to give an amalgam; preliminary electrolysis is not used; anodic polarization.

These circumstances are very common, especially when there is a need for higher resolution without higher sensitivity. They are also of interest in theoretical studies, as in the deduction of the equation of the vector polarogram.

Figure 4 shows curves for lead against N HCl taken at various sweep rates; the recordings are made on a paper chart moving at a speed w in the TsLA polarograph, the displacement ΔS being related to the potential change ΔE by

$$\Delta S = \frac{w}{v} \Delta E.$$

Comparison of curves 1 and 2 shows that the peak height increases at low speeds, on account of the greater accumulation of metal in the drop during low-speed operation, as is clear from the following. Let Δt_1 be the time taken to reach the peak at speed v_1 (curve 1), and Δt_2 the same for v_2 (curve 2); then imagine a polarogram recorded with accumulation (no stirring) for a time $T = \Delta t_2 - \Delta t_1$ and rate v_1. Curve 3 shows this, with a slight downward displacement. The total time taken to record curve 3 is Δt_2. Comparison of 2 with 3 shows that the curves recorded at different rates but with equal times have the same height; the slightly smaller height of curve 2 is associated with diffusion of the metal into the drop.

In this case the peak height is governed by the running time Δt, which equals $\Delta E/v$, in which ΔE is the difference between the initial and peak potentials. Reproducibility then demands fixed values for E_i, $E_{\frac{1}{2}}$, and v.

Condition III. Analogous to II, but cathodic polarization.

Sweep rates of 0.95, 3.7, and 14.7 mV/sec were used with Pb (20 mg/liter) against N HCl with $E_i = -0.3$ V, $\Delta E_\sim = 4$ mV, T = U, and sensitivity 1/64; the corresponding wave heights were 73, 68, and 61 mm.

Here again the wave height increases at low rates, but much less than before, because accumulation occurs only over the range between the deposition potential and the peak potential.

Condition IV. The reaction products are ions; anodic polarization.

This gives no increase in sensitivity; it is best used in analysis when high resolution is essential.

Table 3 gives the peak height for Mo (1 mg/liter against a background of citric acid) as a function of sweep rate in anodic polarization ($E_i = -0.7$ V, $\Delta E_\sim = 4$ mV, sensitivity 1/4). Here Mo^{6+} reacts with one electron*. As one would expect, the sweep rate does not affect the height.

*Results obtained by L. N. Vasil'eva.

TABLE 5. Wave Heights for Lead and Cadmium as Functions of Initial Potential (10^{-7} mole/liter, background N HCl, v = 7 mV/sec, $\Delta E_{\sim}$ = 4 mV, T = 10 min, sensitivity 1/4)

E_i, V	H, mm		E_i, V	H, mm	
	Pb	Cd		Pb	Cd
—0.7	140	—	—0.9	135	107
—0.8	133	98	—1.0	138	105

Table 4 gives some results on the effects of initial potential on the height.

Accumulation (with stirring) was used with 0.1 mg/liter Tl against N HCl; the initial potential was −0.8 V, and 20 min gave a lower peak than 10 min (63 and 83 mm respectively), on account of the effects of surface-active materials.

The adsorption was much less with an initial potential of −1.1 V, but some contamination built up in the sweep from −1.1 V.

Table 5 shows that the initial potential has little effect on the height if the background is sufficiently pure.

Theory predicts high resolution in ac polarography provided that the peak for the component is sufficiently far from associated peaks; the resolution is independent of the concentration and of the peak potentials [6]. On the other hand, the practical resolution with the dropping electrode is substantially restricted by the absolute concentrations and potentials. For instance, second-order peaks interfere if the potential lies near the electrocapillarity zero. The polarographic-maximum effect appears, in that the branch of the wave of an associated component lying near the peak it is desired to assay may descend far towards negative currents, with the result that the desired wave may not be seen. Surface-active substances are added to minimize or suppress this effect. High resolution was not used in classical polarography, so it was not difficult to choose a suitable surface-active material; but in ac polarography there is difficulty over both the nature and amount of the material, since reproducible results are essential.

The polarographic maximum arises from tangential motion of the surface during formation and growth, so it is characteristic solely of the dropping electrode. No such maxima occur on stationary drops, so the absolute potential of the peak does not affect the resolution.

We have often observed that clearly separated and undistorted waves on the vector polarogram for a given ratio of two components when the absolute concentration of the unwanted one is high. Here the ohmic resistance of the cell becomes important, as does the increase in the nonsinusoidal component of the current at the anode. It is undesirable for the current density at the anode to exceed 10 $\mu A/cm^2$. The absolute concentrations must be reduced in order to reduce these effects, and this demands an increase in sensitivity.

Accumulation on a stationary drop provides increased sensitivity if the component is a metal that will form an amalgam; no maxima are produced, and sometimes the absolute concentrations can be reduced considerably, with the result that the resolving power may be an order of magnitude higher than that found with the dropping electrode.

Figure 5 shows a vector polarogram from $3.3 \cdot 10^{-7}$ mole/liter of Cd in the presence of $2 \cdot 10^{-3}$ mole/liter of Bi; resolving power is 6000:1. Figure 6 shows 0.1 mg/liter of pure cadmium against ammonia as background (resolving power 20,000:1). These results do not represent the limit; they show that ac polarography on stationary drops gives the highest resolution attainable.

This feature enables one to determine trace impurities in metals without preliminary separation of the base; it also enables one to examine the formation of intermetallic compounds in the amalgam.

Conclusions

1. A study has been performed on the stationary-drop vector polarograph as an analytical instrument. Factors that restrict the resolving power and sensitivity have been examined.

2. Substances that form amalgams (solid phases) on the drop can give sensitivities two orders of magnitude higher than those from dropping electrodes; 10^{-9} mole/liter, or even less, is attainable. Careful purification of reagents and mercury is necessary, especially as regards surface-active materials.

3. It has been found that the resolving power on a stationary drop may be raised to well in excess of ten thousand, which enables one to determine ultramicro amounts of impurity in a metal without preliminary removal of the base.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
