AN AUTOMATIC POLAROGRAPHIC CONCENTRATION METER

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There have been many papers on the theory of ac polarography, and on analytic expressions for ac polarograms (see, for instance, [1-4]). Delahay [5] has given the soundest deduction of equations for ac polarograms. His assumptions were three:

1) that the surface of the cathode does not change,

2) that the ions reach the cathode by linear diffusion, and

3) that the reactions at the cathode are reversible.

Delahay observes that the equations derived in this way can also be used for mercury-drop electrodes.

His equations can be put in the form

$$I(u) = 4I_{max}\frac{e^{-\frac{nF}{RT}(u-u_{1/2})}}{\left[1+e^{-\frac{nF}{RT}(u-u_{1/2})}\right]^2}, \quad (1)$$

where

$$I_{max} = I(u) \text{ for } u = u_{1/2} = \frac{n^2F^2}{4RT} AD^{1/2}\omega^{1/2}E_mC_0. \quad (2)$$

If we insert the numerical values of the gas constant R and of Faraday's number F in the latter, we get

$$I_{max} = 965\cdot 10^6 n^2 AD^{1/2}\omega^{1/2}E_mC_0 = KC_0, \quad (3)$$

where I(u) is the ac current, in μa; I_{max} is the maximum ac current in μa; n is the electron number of the reaction; A is the cathode area, in cm^2; D is the diffusion coefficient for the ions, in cm^2sec^{-1}; ω is the angular frequency, in radians/sec; E_m is the ac voltage, in volts; C_0 is the initial concentration of the solution, M; u is the dc voltage, in volts; $u_{1/2}$ is the half-wave potential, volts; and e is the base of Naperian logarithms.

It is clear from (1) that the ac current curve passes through maximum as the dc voltage is changed slowly. This maximum current, I_{max}, is proportional to C_0, as (2) and (3) show; it occurs at the half-wave potential of a normal polarogram. Theory [6, 7] indicates that the half-wave potential is independent of concentration, and depends only on the nature of the substance.

Thus, the ac current polarogram gives qualitative and quantitative data on a one-component solution (Fig. 1). The curve shows several peaks if the solution contains several substances; each peak gives the concentration and nature of one component (Fig. 2).

The dc voltage applied to the cell must be varied, and the ac current measured, in order to analyze the solution in this way. But (1) and (3) imply that, if the natures of the components are known, it is possible to set the voltage at the half-wave potential. The ac current will then vary with the concentration. The concentration can be measured continuously if I_{max} is recorded. The device becomes a recording concentration meter.

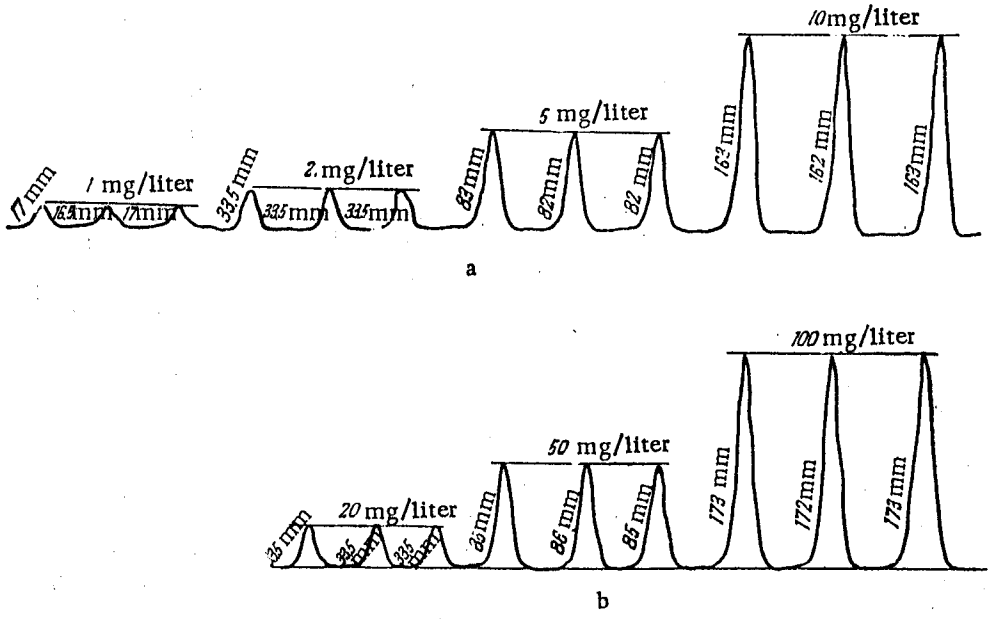

Fig. 1. Cadmium polarograms taken on a background of 1 N Na_2SO_3: a) 1, 2 and 5 mg Cd/liter; b) 20, 50 and 100 mg Cd/liter.

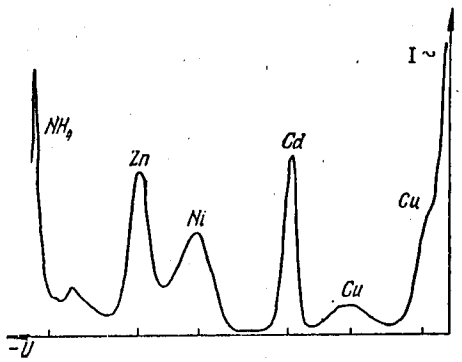

Fig. 2. Polarogram of a solution containing 20 mg/liter of copper, cadmium, nickel and zinc; background of 1 N $(NH_4)_2SO_4$ + + 1 N NH_4OH.

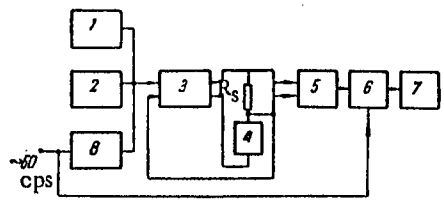

Fig. 3. Block diagram of the concentration meter: 1) source of linearly varying voltage; 2) dc voltage source; 3) balancing unit; 4) cell; 5) ac amplifier; 6) phase-sensitive detector; 7) recorder; 8) phase-shifter.

If a full polarogram is run, all factors except the dc voltage are kept constant. The ac and dc voltages are kept fixed during continuous analyses.

We have developed a recording polarographic concentration meter which uses ac with a sinusoidal waveform.

The apparatus (Figs. 3 and 4) can be used as a concentration meter, or as an ac polarograph.

In the first case the head (Fig. 5) is a thermostatic polarography cell, through which the solution passes continuously.

In this instrument the polarogram is simply the curve of the in-phase ac current against the dc voltage. The cell that is used for ac polarography is a normal polarography cell.

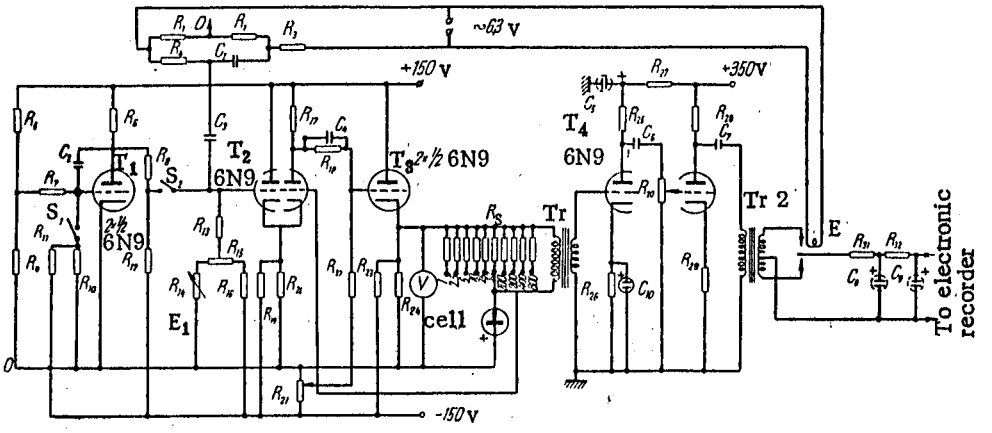

Fig. 4. Theoretical circuit of the concentration meter: R_1 = 5 ohm, R_2 = 5 ohm, R_3 = 3.3 kohm, R_4 = 1 kohm, R_5 = 200 kohm, R_6 = 0.5 meg, R_7 = 10 meg, R_8 = 1.6 meg, R_9 = 5.1 kohm, R_{10} = 1.3 kohm, R_{11} = 82 kohm, R_{12} = 2.2 meg, R_{13} = 100 kohm, R_{14} = 10 × 150 ohm, R_{15} = 200 kohm, R_{16} = 68 kohm, R_{17} = 0.51 meg, R_{18} = 2 meg, R_{19} = 150 kohm, R_{20} = 10 kohm, R_{21} = 100 kohm, R_{22} = 2.2 meg, R_{23} = 56 kohm, R_{24} = 1 kohm, R_{25} = 0.51 meg, R_{26} = = = 3.3 kohm, R_{27} = 100 kohm, R_{28} = 51 kohm, R_{29} = 1 kohm, R_{30} = 1.5 meg, R_{31} = 150 ohm, R_{32} = 150 ohm; C_1 = 1 μf, C_2 = 10 μf, C_3 = 0.25 μf, C_4 = 1 μf, C_5 = 10 μf, C_6 = 0.05 μf, C_7 = 2 μf, C_8 = 3000 μf, C_9 = 3000 μf, C_{10} = 100 μf.

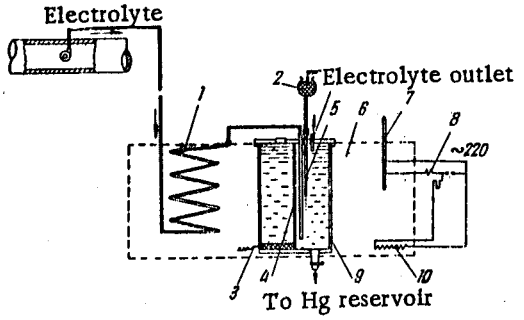

Fig. 5. The cell used in the polarographic concentration meter: 1) coil of tubing; 2) cathode; 3) anode; 4) filter; 5) capillary; 6) thermostat; 7) contact thermometer; 8) MKU-48 relay; 9) cell; 10) heater.

A linear-sweep generator (tube T_1 in Fig. 4, which acts as an integrator) provides the slowly varying voltage. The output from the generator passes to a stabilizer (designed around tube T_2). The sweep generator is switched out when the unit is used to measure concentrations, and the voltage on the cell is set with the voltage divider R_{14} and R_{15} (coarse and fine controls).

The ac supply is taken from the 50 cps line. The cell is supplied via a phase-shift network (R_1, R_2, R_3, R_4 and C_1) and via a voltage stabilizer, T_2 and T_3.

One of the standard resistors R_S is connected in series with the cell; the current is measured in terms of the voltage drop across the resistor. The ac and dc currents both pass through this resistor. The two increase together when the concentration rises, and,hence,so does the voltage drop across R_S. The ac component is used to measure the current. However, the increased voltage drop across R_S will cause the voltage across the cell to fall unless suitable measures are taken; and this fall would cause the ac component to alter. The readings would then depend on the dc voltage. The ac and dc voltages are kept constant (stabilized), in order to reduce the effect on the sensitivity. Voltage stabilizers are used for the purpose.

The stabilizer built around T_2 and T_3 is a dc amplifier with 100% feedback. The left and right halves of T_2 are coupled via the common cathode load R_{20}. The ac and dc voltages are applied to the left grid. The right grid is used to apply negative feedback to the cell.

The two halves of T_3 work in parallel as a power amplifier and have an output impedance of about 20 ohm.

The ac component of the voltage drop across R_S is amplified by the two-stage amplifier T_4; the output is fed to a phase-sensitive detector (an electromechanical vibrator, E). This detector is combined with a phase-shift circuit to differentiate between the in-phase and out-of-phase ac components.

The output from the detector passes via an RC filter to an electronic recorder (the RC filter smooths out the current fluctuations when a dropping-mercury electrode is used).

A special power unit supplies all the voltages in stabilized form.

TABLE 1

Readings of Concentration Meter and Heights of Peaks as Functions of Cadmium Concentration (background 1 N Na_2SO_3)

Concentration, mg/liter	Height of ac peak, scale divisions	Meter reading for concentration in divisions (full scale = 10 divisions)
1	0.65	0.65
2	1.35	1.4
5	3.4	3.5
10	7.0	7.1
10	0.65*	0.65*
20	1.35	1.35
50	3.5	3.6
100	7.2	7.4

*Sensitivity reduced by a factor of 10.

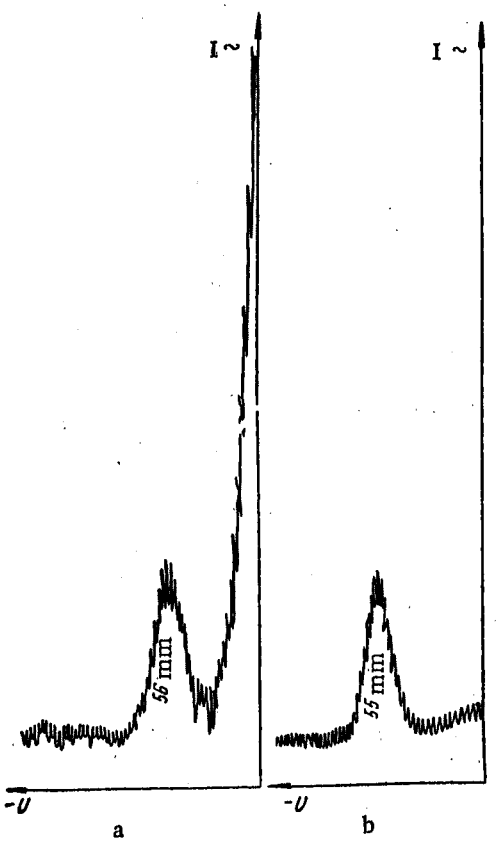

Fig. 6. Polarograms of 1 mg/liter of cadmium with and without copper; background 1 N $(NH_4)_2SO_4$ + 1 N NH_4OH.

A prototype instrument was made up to this design, and was tested in the laboratory, and under industrial conditions.*

The uses of the instrument for ac polarography and as a concentration meter were checked.

In the first case we ran full ac polarograms of standard solutions with various concentrations, and compared the peak heights; in the second, we took only the readings given when the instrument was set at the half-wave potential for the element and various solutions of known concentrations were run into the cell. Table 1 gives the results.

The polarograms (Fig. 1) also show that the results were reproducible.

We estimated the resolving power by using small amounts of a material in the presence of large amounts of a more positive one. Figure 6 shows 1 mg/liter of cadmium (a) in the presence of 200 mg/liter of copper, and (b) without copper.

The results showed that the readings were reasonably reproducible. The reduced error in complete polarograms did not exceed 1.5%; and that in concentration measurements at fixed half-wave potentials, 2.0%.

The apparatus was also tested in the leaching shop at the "Elektrotsink" factory. The zinc electrolyte (freed from copper and cadmium) was checked for residual cadmium.

*V.D. Emel'ianov, mechanic in the Tsvetmetavtomatika workshops, took an active part in making and adjusting the prototype polarograph.

TABLE 2

Data Given by the Concentration Meter under Industrial Conditions Compared with Those Given by a TsLA Laboratory Polarograph

Meter reading, mg/liter (10 mg/liter, full scale)	Concentration given by the TsLA polarograph (mg/liter)
3.9	3.9
5.3	5.0
6.1	6.0
4.7	5.0
1.5	1.5
7.5	7.4
4.5	4.1
2.4	2.1
4.8	4.5
6.4	6.0

The technical requirements were that the purified electrolyte should contain not more than 5 mg of cadmium per liter. The tests were done as follows.

The purified electrolyte was sampled by a pump that passed part of the solution to the polarograph. The solution passed through a coil in a thermostatic water-bath (temperature constant to ±1°C) and flowed at 150 cc/min to the cell. Previous tests had shown that flows in the range 0 to 250 cc /min did not cause the readings to change by more than ±2%. The readings became unstable at very high flow rates. The voltage was set at the appropriate half-wave potential, and the instrument was calibrated from a laboratory polarograph that used the TsLA system.

The readings were checked against periodic laboratory analyses. Table 2 gives some of the results.

It is clear that the two sets of data show a divergence that does not exceed ±4% in reduced error terms.

This level of error is usually quite acceptable for continuous measurements of such small concentrations directly at the process plant.

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A VISUAL SQUARE-WAVE POLAROGRAPH

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We have made a visual square-wave polarograph in which the capacitative currents are balanced electronically. The method improves the sensitivity of analyses by square-wave polarography [1]; the apparatus can be used to record square-wave and normal polarograms simultaneously. No circuit for balancing the capacitative currents has been described [2]; we have developed the main part of the device (the electronic switch) ourselves [3].