INSTRUMENTS AND LABORATORY TECHNIQUES

A NEW OSCILLOGRAPHIC POLAROGRAPH MODEL

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We developed and constructed a new model of the cathode-ray polarograph which can be used for the determination of small concentrations of elements and organic compounds, for the measurement of capacitance of electric double layers on drop and solid electrodes, of impedance of electrolytic cells, and of the rate and reversibility of electrode reactions, as well as in studies of adsorption and surface phenomena. The instrument secures an accuracy of ±2% for concentrations from 10^{-3} to 10^{-5} molar and of ± 3% for concentrations from 10^{-6} to 10^{-7} molar.

In comparison with the existing models*, the proposed model has the following characteristics.

A circuit providing periodical as well as slave scanning with different fixed rates of change of the potential was used. Such operating conditions permit the use of mercury drop electrodes as well as mercury electrodes, the surface of which is 200-300 times larger than the surface of a mercury drop. The sensitivity of the method is thereby greatly increased. Periodic scanning permits the use of solid electrodes, in particular, cylindrical electrodes, which is important in automatic production control.

Sensitivity of the Instrument

Switch positions	Load resistance, ohm	Instrument sensitivity μa/mm
1	50	16.78
2	100	8.39
3	150	5.59
4	250	3.36
5	500	1.68
6	1000	0.84
7	2000	0.42
8	5000	0.168
9	10000	0.084
10	15000	0.056
11	20000	0.042

The polarograph circuit provides the possibility of simultaneously using two cells which are switched by means of a polarized relay. This is very promising for the quantitative determination of substances by titration.

A constant negative voltage and a positive sawtooth voltage with a fixed amplitude are simultaneously fed to the polarograph cell. Under such polarization conditions, distortions of the current intensity vs. voltage curves by capacitance currents are almost eliminated and the sensitivity of the method is increased, since, for a negative voltage exceeding the reduction voltage of the substance under investigation, the substance accumulates on the electrode.

Polarization by negative sawtooth voltage by means of switching the poles of the electrolytic cells is also provided.

The electronic circuit of the oscillographic polarograph, which is based on the 13LO-36 electron-beam tube, consists of the following basic units (Fig. 1): a generator of linearly changing voltage; a compensator for the influence of the load resistance of the cell and a capacitance current compensator; a synchronizer and kipp oscillator for the pulse delay, which is synchronized with the dripping period of mercury; an amplifier for the vertical beam deflection; an amplifier for the horizontal beam deflection; a feed unit.

* Ya. P. Gokhshtein, S. V. Kuz'man, A. F. Volkov and V. A. Yanchevskii, Zavodskaya Lab. 23, 8, 988 (1957); P. Delahay, New Instrumental and Methods in Electrochemistry [Russian translation] (IL, 1957) pp. 427-432.

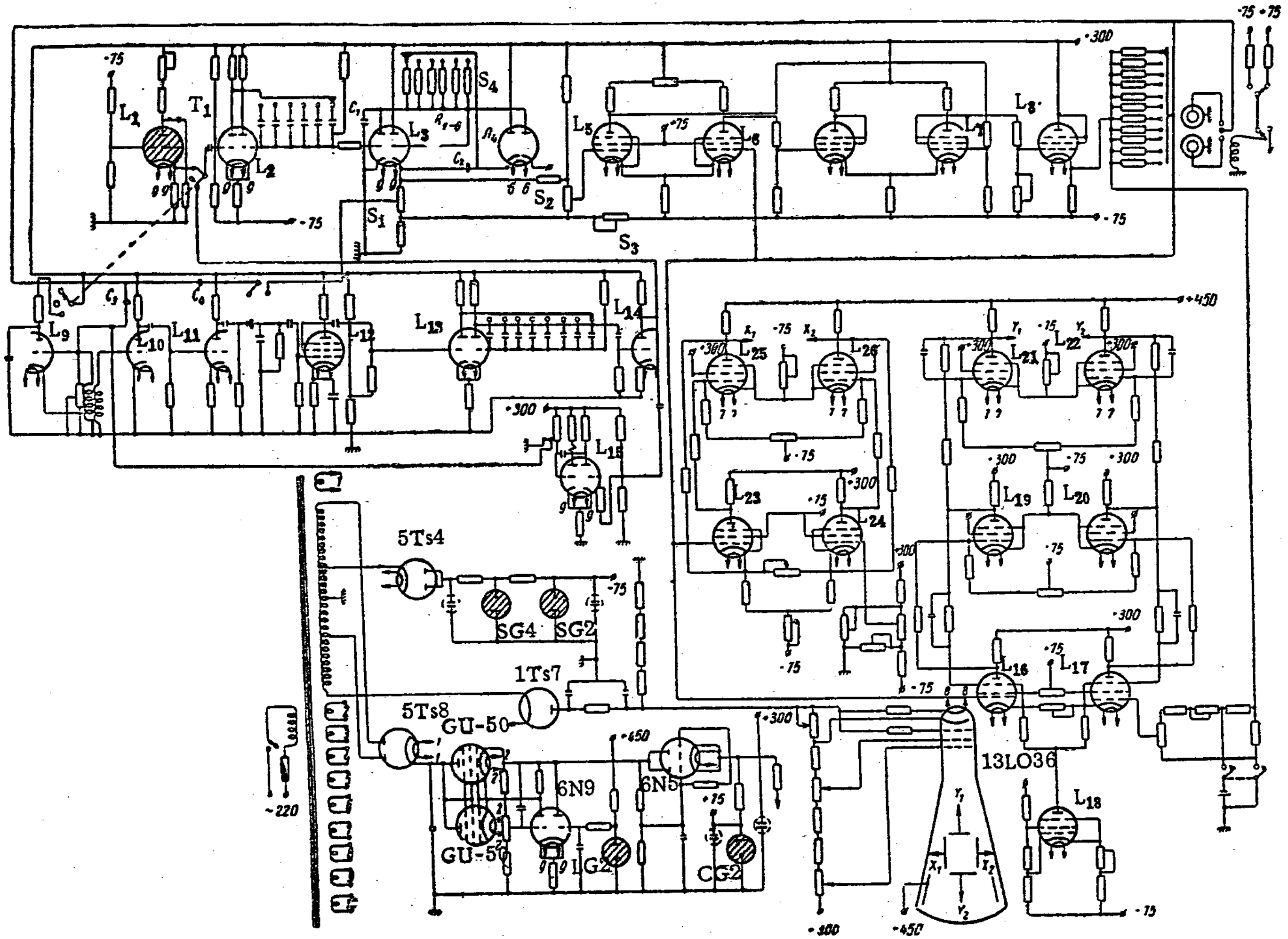

Fig. 1. Electronic circuit of the oscillographic polarograph.

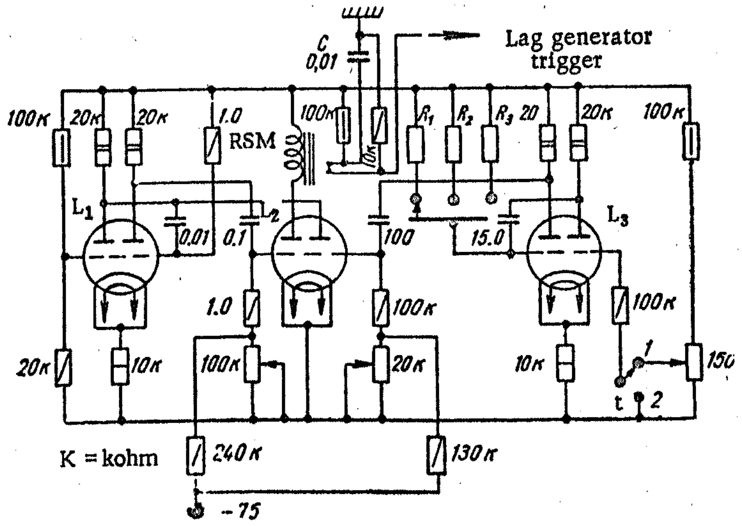

Fig. 2. Synchronization circuit with controlled dripping.

The generator of linearly changing voltage serves for feeding a sawtooth voltage to the cell and for horizontal scanning of the screen. The generator must secure a high degree of linearity of the voltage fed to the cell. For this purpose, a circuit where the capacitor is charged with direct current has been selected which permits the production of linearly changing voltage with deviations not exceeding 1% and secures a good use of the feed voltage (for 300 v, voltages with an amplitude of the order of 200 v can be obtained).

The circuit can operate under periodic operating conditions as well as under slave-sweep conditions. The following rates of change of the potential v have been obtained in operation under slave-sweep conditions: 2.5, 4.8, 9.5, 20.3, 36.4, and 73.3 v/sec. The sawtooth voltage amplitude is 0.744 v. In periodic scanning, the following rates of change of the potential were obtained: 2.8, 5.0, 10.0, 20.6, 38.2, and 74.7 v/sec.

The rates of the voltage change were determined by means of an N-10 magnetoelectric loop oscillograph. When the circuit is switched to periodic operation (toggle switch t_1 is in position "Periodic"), a positive pulse, the amplitude of which is equal to $\sim$20-25 v, is tapped off the cathode of thyratron L_1 (TG1-0.1/0.3). The pulse triggers the kipp oscillator L_2 (6N8). The negative voltage drop is fed to the left half of L_3 (6N8), which is normally open, after which its anode voltage is close to the ground potential. From the moment the supply of current through the left half of L_3 is interrupted, its anode voltage begins to rise with the time constant, which is determined by the capacitance C_1 and resistances R. The magnitude of R is regulated in steps from R_1 to R_6 in dependence on the position of switch S_4. The capacitor C_1 is connected to the grid of the cathode follower (the right-hand half of L_3). A variation of the grid voltage causes a change in the cathode voltage and, consequently, a change in the voltage of the right-hand half of the L_4 cathode. The diode L_4 (6 × 6) is closed as soon as its cathode voltage starts to rise. In order to obtain a good linearity, it is necessary that the intermediate capacitor C_2 releases only a small portion of the stored energy during one period, i.e., that C_2 be greater than C_1. Usually, a ratio $C_2 > 20\ C_1$ is chosen. In this circuit, C_2 is 150 times greater than C_1. The second half of L_4 is used as a limiter for the production of sawtooth voltage of constant amplitude.

The generator circuit supplies a linearly changing voltage to the unit compensating the difference of the cell load resistance. For the purpose of compensating the cell capacitance current, its linear voltage is fed through capacitor C_4 (1000-1500 $\mu\mu$f) to potentiometer P_1, which regulates the voltage necessary for this compensation.

The load resistance compensator is intended for maintaining the assigned magnitude of steady voltage and for preserving the linearity of the sawtooth voltage independently of changes in the cell impedance during the process of the drop growth.

The voltage tapped off the divider in the cathode of L_3 is fed through potentiometer P_2 to the grid of L_5 (12Zh1L), and the voltage tapped off the cell is fed to the grid of L_6 (12Zh1L). The cathodes of tubes L_5 and L_6 are connected. The anode voltage in L_5 is a function of the voltage difference applied to the grid of these tubes

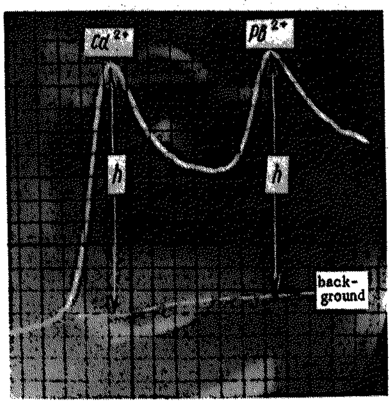

Fig. 3. Oscillogram of a 1 N solution of KCl containing 5.0 γ/ml of Cd^{2+} and 5.0 γ/ml of Pb^{2+}. Slave sweep $K_{ampl} = 10$; $\alpha = 4.8$ v/sec; $U_{=} = -1.1$v.

and it tends to keep the cell voltage constant during the growth of the drop. The anode voltage is determined by potentiometer P_2. The degree of stability of the cell voltage during the drop growth is determined by the amplification of the feedback loop and by the change in the cell resistance. The voltage from the L_5 anode is fed to L_7 (12Zh1L), and from the anode of the latter, to the cathode follower L_8 (12Zh1L).

The steady cell voltage is established by potentiometer P_2; it can vary from +0.1 to −2.3 v. By means of potentiometer P_3, the voltage can be shifted within a small range, toward the region of positive as well as toward the region of negative potentials. The circuit of potentiometer P_2 is constructed in such a manner that, when the cell voltage changes within the indicated limits, the amplitude of the linearly changing voltage remains constant with an accuracy of 0.5%. The sensitivity of the instrument is determined by load resistances of the cell (see table).

The synchronizer and the lag kipp oscillator. The synchronizer circuit triggers the generator of linearly changing voltage after the drop detaches itself. The lag kipp oscillator serves for producing an oscillogram on the screen at a given moment of the drop lifetime. The sinusoidal voltage generator L_9 (1/2 6N8) is connected to the cell through capacitor C_3. At the moment when the drop is detached and the cell impedance is at a minimum, the generator starts to oscillate and a voltage drop arises across capacitor C_3. The voltage drop is transmitted through the amplifier (L_{10} and L_{11}) (1/2 6N8) and, after being detected and amplified in L_{12} (6Zh2P), it connects the lag kipp oscillator L_{13} (6N8). The differentiated trailing edge of the pulse supplied from L_{13} triggers the generator of linearly changing voltage (t_1 is in position "Slave sweep") after passing through the amplification cascade L_{14} (1/2 6N8). The relay in the anode of kipp oscillator L_{15} (6N8) stops the oscillations of the sinusoidal voltage generator for the duration of the sweep after the drop detaches itself. The influence of high-frequency oscillations on electrolysis is thereby eliminated. The time constant $\tau \approx 1$ sec. The lag time in the operation of the generator of linearly changing voltage is determined by the duration of pulses supplied by the lag kipp oscillator L_{13} and can have 10 fixed values from 0.005 to 23 seconds, depending on the switch position. The time instability does not exceed 3% and is mainly determined by the instability of the grid voltage.

The spontaneous detachment of the drop serves for triggering the slave sweep kipp oscillator in the above high-frequency sysnchronizer. A synchronizing scheme with controlled dripping also can be used (Fig. 2). Synchronization is achieved by means of a signal simultaneously supplied to the kipp oscillator and to the relay which detaches the drop. The necessity for the generation and feed of high-frequency oscillations to the drop is thereby eliminated.

In switching over to single sweeps (toggle switch t_1 is in position "Slave sweep"), a rectangular voltage of a duration corresponding to the tripping period is fed from the anode of the left half of tube L_3 to the differentiating circuit. The leading front pulse is fed to the grid of the right-hand half of tube L_2 and, after amplification, triggers the kipp oscillator based on tube L_1. The positive pulse of the kipp oscillator, supplied from the anode of the right -hand half, is fed to the grid of the left-hand half of tube L_2, to the anode of which an RSM relay with striking pin fastened to its armature is connected. When the relay operates, the pin strikes the capillary and the drop falls off. At the same time, capacitor C, discharging through a resistance of 10 kohm, triggers the slave sweep kipp oscillator. Resistances R_1, R_2, and R_3 are chosen in dependence on the dripping period of the mercury electrode.

The vertical beam deflection amplifier is based on seven tubes with two feedback loops. It amplifies the cell current until the intensity necessary for observing it on the screen is attained. The amplifier circuit must secure the following: a high-degree of linearity of the amplitude characteristic, stability, and input tube grid currents which are small and stable in time.

The input tubes L_{16} and L_{17} (12Zh1L) have a commonly cathode resistance for which a pentode L_{18} (12Zh1L) is used. Such a circuit secures a good compensation of the linearly changing voltage on the anodes of tubes L_{16}

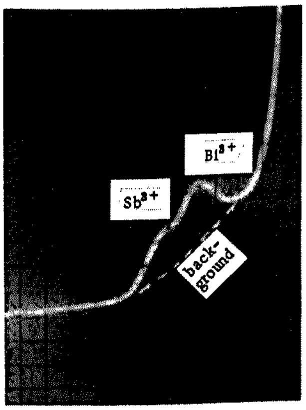

Fig. 4. Oscillogram of a 1 N solution of HCl containing 0.5 γ / ml of Sb^{3+} and 0.5 γ / ml of Bi^{3+}. Slave sweeps; $K_{ampl} = 8$; $U_= = -0.49$ v/sec; $\alpha = 2.5$ v/sec.

and L_{17}, since the internal resistance R_i of the pentode has a magnitude of approximately 1 mohm, and its direct current resistance is sufficiently small.

The first feedback loop covers tubes L_{16}, L_{19}, L_{17}, and L_{20} (12Zh1L), and the second loop covers the output push-pull cascades L_{21} and L_{22} (6Zh4). The capacitors connected in parallel to the resistors in the negative feedback cut off the high frequencies, thereby reducing the noise. The amplification factor is $3.9 \cdot 10^3$. If the line voltage changes by $-10 + 5\%$, the instability of the amplification factor does not exceed 1%. The nonlinearity of the amplitude characteristic does not exceed 0.5%. The zero drift after a warm-up period of half an hour is not greater than 1 mv/hr. The transmission band is from 0 to 1000 cps.

The horizontal beam deflection amplifier secures the necessary scanning in the electron-beam tube. In order to increase the operational stability of the horizontal deflection amplifier, which consists of tubes L_{23} (12Zh1L), L_{25} (6Zh4), L_{24} (12Zh1L), and L_{26} (6Zh4), feedback from the anodes of the output tubes to the cathodes of the input tubes is provided. The first cascade is based on a paraphase amplifier circuit. The second cascade, which is connected to the deflecting plates of the electron-beam tube, is based on a push-pull circuit. The amplification factor is 300. The transmission band is 50,000 cps. For a variation of line voltage of $-10 + 5\%$, the instability of the amplification factor does not exceed 1%. The nonlinearity of the amplitude characteristic does not exceed 0.3%. The zero drift after one hour operation and a warm-up period of half an hour, does not exceed 1.6 mv/hour.

Feed unit. Stabilized voltage is fed to all units of the polarograph in order to increase the stability in operation. The feed unit supplies the following voltages to the circuit:

1) a stabilized voltage of +450 v where the instability for a line voltage variation of $-10 + 5\%$ does not exceed 0.1%;

2) a stabilized voltage of +300 v where the instability for a line voltage variation of $-10 + 5\%$ does not exceed 0.05%;

3) a stabilized voltage of +75 v where the instability for the above-indicated variations of the line voltage does not exceed 0.05%;

4) a stabilized voltage of -75 v where the instability does not exceed 0.1%;

5) a tube feeding voltage of -2500 v.

In order to increase the operational stability of the instrument and to reduce alternating current inductions, a stabilized voltage of +300 v from a rectifier is fed to the filaments of tubes 12Zh1L.

For the operation of two polarographic cells, a polarized RP-4 relay is introduced, which at a frequency of 400 cps periodically connects cells 1 and 2 to the load resistance.

Figures 3 and 4 illustrate the instrument operation when a slave sweep with a lag of 5 seconds after the drop detaches itself is supplied to the cell. The oscillogram (Fig. 3) shows the electrolysis of 1 N solution of KCl containing 5.0 γ/ ml of Pb^{2+} and 5.0 γ/ ml of Cd^{2+}. For -0.65 and -0.44 v on a relatively saturated calomel electrode, well-defined peaks of cadmium and lead, the maximum current intensity of which was not distorted by the capacitance current, appeared on the curve. Therefore, the instrument permits an accurate determination of the actual values of Cd^{2+} and Pb^{2+} currents when they are both present.

The selectivity and the sensitivity of the oscillographic polarograph can be seen in the case where Bi^{3+} and Sb^{3+} in a solution of hydrochloric acid were simultaneously determined (Fig. 4). In spite of the nearness of the potentials of bismuth and antimony half-waves on the volt-ampere curve, the waves for bismuth and

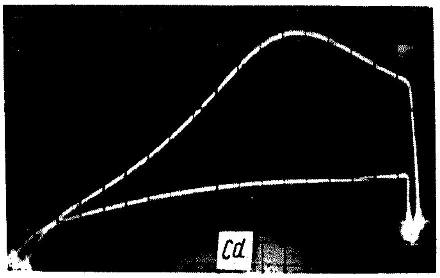

Fig. 5. Oscillogram of the background and of a 1N solution of KCl containing 0.1 γ/ml of Cd^{2+}, obtained with two equal cylindrical platinum electrodes. Slave sweeps; $K_{ampl} = 10$; $\alpha = 20.6$ v/sec; $U_{=} = -0.49$ v.

antimony can be clearly seen (the potentials of Sb^{3+} and Bi^{3+} half-waves differ by ~ 40 mv). The oscillogram was obtained for a 1N solution of hydrochloric acid containing 0.5 γ/ml of Sb^{3+} and 0.5 γ/ml of Bi^{3+}.

Figure 5 illustrates the simultaneous operation of the instrument for two electrolytic cells having two cylindrical platinum electrodes of equal surface area. The curves on this oscillogram were obtained for the background (1 N KCl) and for a 1 N solution of KCl containing 0.1 γ/ ml of Cd^{2+}.

The instrument is characterized by a high stability and reproducibility of readings.

THE DFS-10 MULTICHANNEL PHOTOELECTRIC DEVICE FOR EMISSION SPECTRAL ANALYSIS

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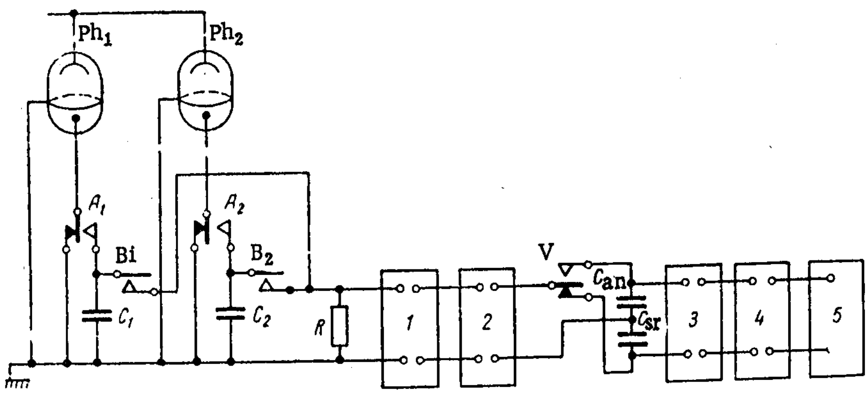
The DFS-10 instrument consists of a multichannel device with photoelectric recording of individual spectral lines and is intended for the rapid quantitative spectral analysis of metals and alloys.



Schematic diagram of the instrument. 1) Amplifier; 2) limiting device; 3) v-t voltmeter; 4) feed unit; 5) recording device.

Thirty-six exit slits for the separation of 36 spectral lines are provided in the device. A light receiver is placed behind each slit. For simultaneous operation, a special programming device permits the use of any previously selected combination of twelve spectral lines. An over-all number of twelve such combinations can be secured by the programming device. Thus, using one of the exit slits for the comparison line in each combination, the presence of eleven elements in the specimen under investigation can be determined.