

The development of polarographic apparatus is proceeding in two directions, i.e., for analytical use and for scientific research. In some polarographs these functions are combined either through the complication of the design of the instrument by the introduction of additional modes of operation or through the utilization of the broad possibilities of the method employed in the instrument. An example of the latter is the high-frequency polarograph, which can be used both for the investigation of electrode processes [1, 2, 7] and for analytical work [3, 4].

The detector polarograph has been developed in our Institute. The name of the instrument arises from the fact that the electrode-solution boundary in the polarographic cell exhibits detector characteristics when a high-frequency potential is applied to it. The current i passing through the cell can be represented as the sum of constant and harmonic components, each of which bears information on the concentration of the substance in the solution, its nature, and the character of the electrode reaction. If the high-frequency potential is modulated with a low frequency, the current in the cell will also contain a component at the frequency of the modulating potential $i_{\Delta\omega}$. In view of the fact that the amplitude of this component will be greater than the amplitudes of the other harmonics, it is convenient in the design of high-frequency polarographs to measure $i_{\Delta\omega}$. This principle is also utilized in the detector polarograph at the All-Union Scientific-Research Institute for Ferrous Metallurgy.

The instrument was constructed on the basis of the vector polarograph at the Central Laboratory of Automation [5, 6] and can also operate under vector conditions. Figure 1 shows a block diagram of the instrument.

The polarograph has three fixed frequencies of high-frequency potential: 6.25 kHz, 100 kHz, and 1.6 MHz, which are generated by high-frequency oscillators 1, 2, and 3. The high-frequency potential is modulated by the low-frequency potential in the modulators 4, 5, and 6. The modulation frequency is 50 Hz, and the modulation index is 100%.

After amplification by the amplifiers 7, 8, and 9 the modulated high-frequency potential passes through the ballast capacitor C to the polarographic data unit. The amplitude of the high-frequency potential can be varied over a wide range by means of knobs for the discrete and fine variation of the potential amplitude. The ballast capacitor C serves to stabilize the cell current and, consequently, the potential at the double layer during variation in both the resistance of the supporting electrolyte and the frequency of the high-frequency potential over wide ranges. At the same time a polarizing potential is applied to the cell by means of sources of initial 10 and linearly varying 11 potentials through the compensator 12 and the measurement resistance.

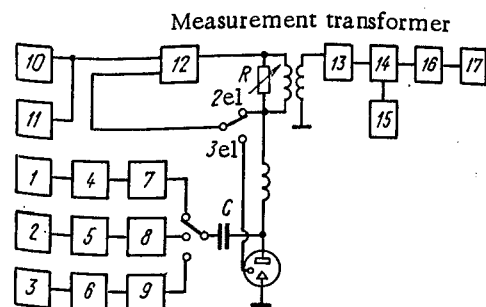


Fig. 1. A block diagram of the detector polarograph.

The useful signal is taken from the resistor R and fed through the measurement transformer first to the amplifier 13 and then to the phase detector 14, operating at the modulation frequency. The reference voltage is applied to the second input of the phase detector from the control cascade 15. From the output of the phase detector the signal passes to the filters 16, which smooth the pulsations of the signal with a frequency of 50 Hz. The high-frequency polarogram is then recorded by the self-recorder 17.

The high frequency unit consists of three independent high-frequency channels of 6.25 kHz, 100 kHz, and 1.6 MHz. (Fig. 2).

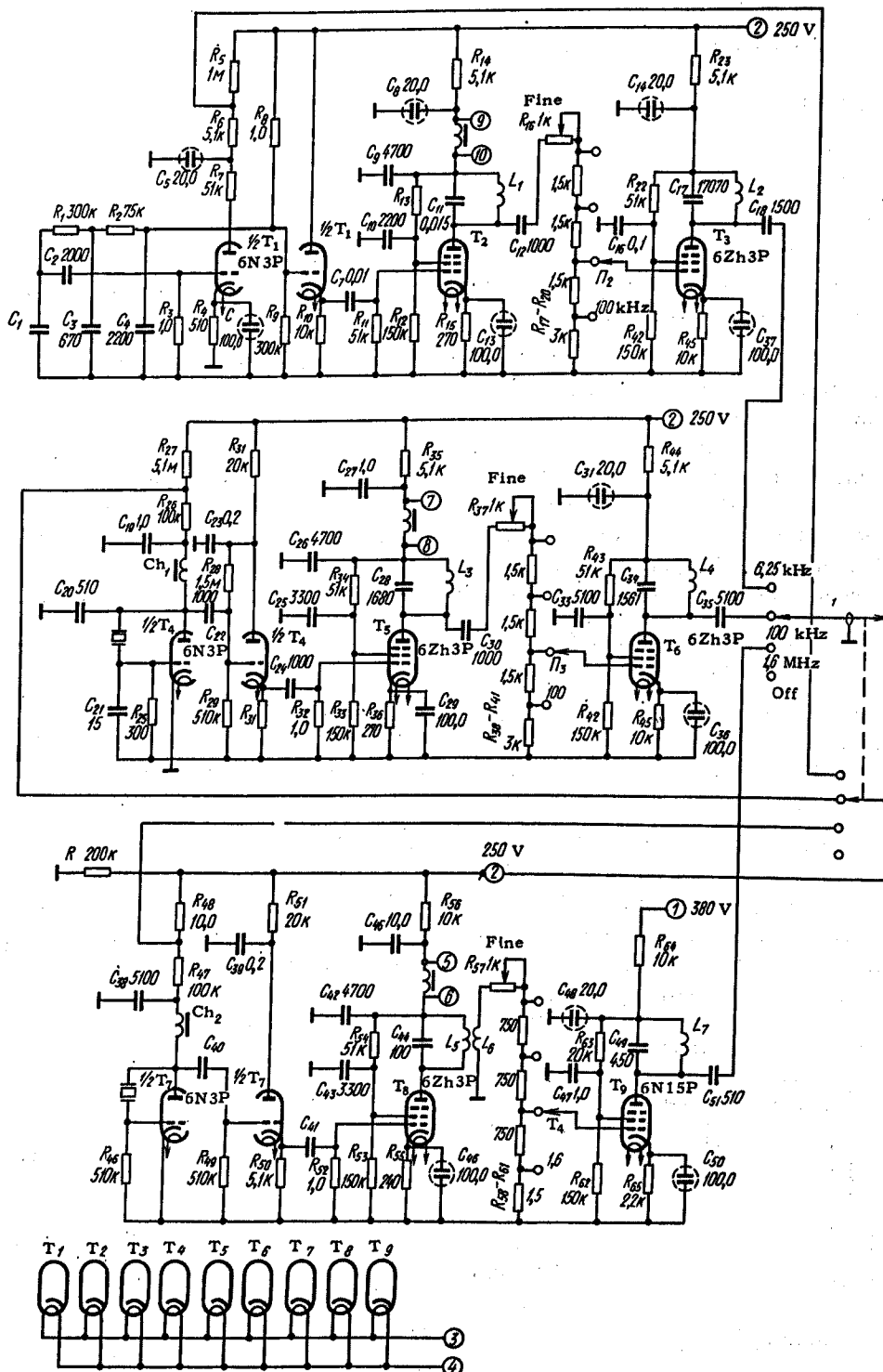


Fig. 2. A line diagram of the high-frequency unit.

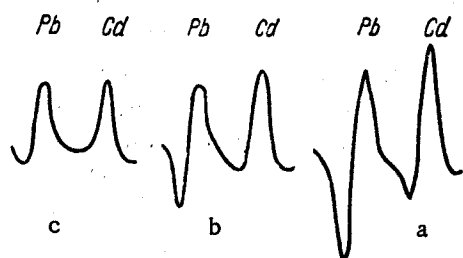


Fig. 3

Fig. 3. The high-frequency polarograms for cadmium at a concentration of $5 \cdot 10^{-6}$ mole/liter in 1 N hydrochloric acid at frequencies: a) 6.25 kHz; b) 100 kHz; c) 1.6 MHz.

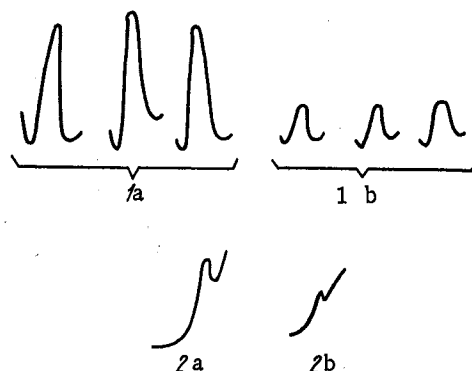


Fig. 4.

Fig. 4. The polarograms for cadmium with 1 N hydrochloric acid as supporting electrolyte: 1) high-frequency polarogram at 6.25 kHz; a) $5 \cdot 10^{-7}$ mole/liter cadmium; b) $2 \cdot 10^{-7}$ mole/liter cadmium; 2) vector polarograms: a) $5 \cdot 10^{-7}$ mole/liter cadmium; b) $2 \cdot 10^{-7}$ mole/liter cadmium.

The 6.25-kHz channel is built around tubes T_1-T_3 (6N3P, 6Zh3P, 6Zh3P). An RC oscillator is connected to the first half of T_1 and a cathode repeater to the second half. The cascade at T_2 serves as modulator. The signal from the tuned circuit $C_{11}L_1$ passes through the divider $R_{17}-R_{20}$, R_{16} to the grid of the output cascade at T_3 , on the anode of which there is also a tuned circuit $C_{17}L_2$. From the latter the signal passes through the switch S_1 to the data unit. When the channel is disconnected, the anode of the first half of T_1 is connected to 250 V through 1 m Ω .

The 100-kHz channel is built around tubes T_4-T_6 (6N3P, 6Zh3P, 6Zh3P). The first half of T_4 is connected to an oscillator with capacitive feedback, where the inductance between the grid and the anode is replaced by quartz.

On the second half of T_4 there is a cathode repeater and on T_5 a modulator with tuned circuit $C_{28}L_3$, from which the high-frequency potential modulated by a potential with a frequency of 50 Hz passes through the divider R_{37} , $R_{38}-R_{41}$ to the grid of the output tube T_6 . From the tuned circuit $C_{34}L_4$ the potential passes through the switch S_1 to the data unit. When the channel is disconnected, the anode of the first half of T_4 is connected to 250 V through 5.1 m Ω .

The 1.6-MHz channel is built around tubes T_7-T_9 (6N3P, 6Zh3P, 6P15P). The first half of T_7 is connected to an oscillator similar to the oscillator at T_4 . On the second half of T_7 there is a cathode repeater. From the secondary winding L_6 of the tuned circuit $C_{44}L_5$ of the modulator L_8 the signal passes through the divider $R_{58}-R_{61}-R_{57}$ to the grid of the output tube T_9 . From the tuned circuit $C_{49}L_7$ the high-frequency potential passes through the switch S_1 to the data unit. When the channel is disconnected, the anode of the first half of T_7 is connected to 380 V through 10 m Ω . A modulating potential of amplitude 110 V and frequency 50 Hz is fed to the anodes of the modulator tubes direct from separate windings on the power transformer.

A stabilized anode feed of 250 V is fed to tubes T_1-T_8 . The stabilizing cascade is built around 6P3S and 6Zh3P tubes and an SG4S stabilitron. An unstabilized supply at 380 V is fed to tube T_9 . All the tubes are fed with an alternating potential, and the heaters are connected in parallel. A special toggle switch TS_2 in the high-frequency cascade supply unit serves to disconnect the anodes of the tubes. A toggle switch TS_1 serves to connect the unit to the supply line.

The unit is fed from an alternating-current supply line of 220 V, 50 Hz. The required power is 75 VA. A current generator regime is realized in the instrument for supplying the cell with high-frequency potential.

A ballast capacitor of $C = 56$ pF, which is intermediate between the high-frequency unit and the data unit, is used to create this regime. In order to reduce the effect of stray capacitances in the cable this capacitor is placed directly at the data unit.

Owing to the use of a current generator regime in the instrument and also to the use of a capacitive ballast potential for these purposes the instrument secures a constant amplitude in the high-frequency potential at the double-layer capacitance over a wide range of variation in the frequencies (from 6.25 kHz to 1.6 MHz) and variation in the resistance of the supporting electrolyte. This provision relieves the operator of the need to calculate the high-frequency

TABLE 1. The Results from the Determination of $K_{1/2}$ and α for Cadmium Solutions

Supporting electrolyte	$K_{1/2}$, cm/sec	α
1 N KCl	2,54	0,78
1 N KNO ₃	3	0,07

potential required from the instrument on passing from one frequency channel to another and also when investigating various solutions which differ in their internal resistances. The instrument secures these functions for resistances up to 500 Ω in the supporting electrolyte with the 1.6-MHz channel and 5 k Ω on the 100-kHz channel.

The high-frequency unit was completed separately. The other functions of the polarograph are fulfilled by the measurement part of the vector polarograph [6], i.e., the formation of the linearly increasing and constant potentials, amplification of the total signal, and isolation of the harmonic component on the modulation frequency.

The instrument was assembled in the form of a desk console with four detachable units. It operates in a unit with a stationary mercury-drop electrode. Figure 3 shows the polarograms for cadmium and lead at a concentration of $5 \cdot 10^{-6}$ mole/liter, recorded on the detector polarograph with various frequencies for the high-frequency potential.

In this form of polarography the polarogram of a reversible reaction is characterized by symmetrical peaks with reference to the zero current level. In the polarography of irreversible reactions a single-humped polarogram is obtained. Accordingly, the polarograms of partially reversible reactions contain two unsymmetrical peaks, the difference in the height of which is greater the lesser the degree of reversibility in the electrode process.

The degree of reversibility decreases with increase in the frequency of the potential supplying the cell, and the polarogram accordingly becomes deformed. This change in the outward form of the polarogram as a function of the frequency of the high-frequency potential is used to calculate the rate constant of the electrode reaction $K_{1/2}$, the transfer coefficient α , and the ion exchange current i_0 [1]. Thus, for cadmium in 1 N potassium chloride and 1 N potassium nitrate as supporting electrolytes, we obtained the results shown in Table 1.

These data agree satisfactorily with those obtained by other authors [1].

In addition the instrument has good analytical characteristics. Figure 4 shows the high-frequency polarograms for cadmium at concentrations of $5 \cdot 10^{-7}$ and $2 \cdot 10^{-7}$ mole/liter with 1 N hydrochloric acid as supporting electrolyte, recorded on the 6.25-kHz channel, and for comparison the vector polarograms recorded with identical conditions in the data unit.

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