

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 $\pm 1^\circ\text{C}$) 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 $\pm 2\%$. 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 $\pm 4\%$ 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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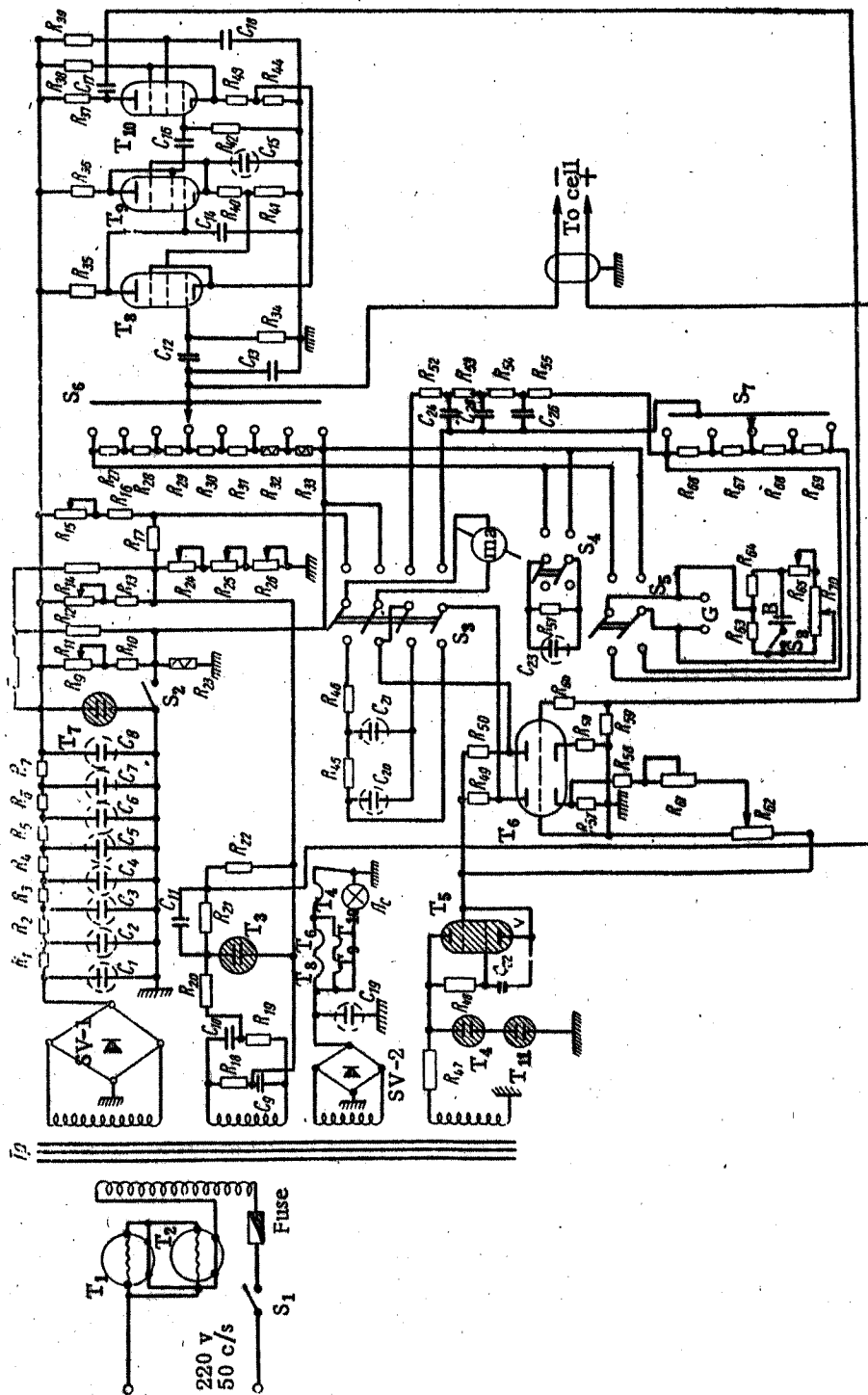
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A VISUAL SQUARE-WAVE POLAROGRAPH

B.Ia. Kaplan and E.N. Ulanovskii

(Chemical Laboratory, Geological Directorate for the Central Regions; Works Laboratory)

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].



Circuit of the polarograph: M) microammeter (100 μ A); B) FBS 0.25 miniature battery; Tp) 60 w transformer, 110/270-22-400-400 V; SV) selenium rectifier.

Some preliminary tests showed that this method gave polarograms that did not differ from those found with sinusoidal waveforms [1]. The electronic balancing improved the sensitivity by $1\text{--}1\frac{1}{2}$ orders of magnitude. Reliable results were obtained with reversibly reducible substances at concentrations of $5 \cdot 10^{-6}$ to 10^{-5} N. The Figure gives the theoretical circuit.

The unit is fed from the 220 v line. Two barretters T_1 and T_2 stabilize the current in the primary of the power transformer.

The bridge rectifier SV-1 operates from the 270 v secondary, and supplies the amplifying tubes and the cell via the RC filter (R_1 to R_7 and C_1 to C_8), and also supplies the voltage stabilizer T_7 .

A KMS three-decade resistance box (R_{24} , R_{25} and R_{26} ; total 99.9 ohms) is used to adjust and read the polarizing voltage. This box replaces the normal potentiometer; it causes the voltage to vary not quite linearly with resistance setting (the deviation is 2% for the range from 0 to 99.9 ohms). Resistor R_{12} allows one to vary the maximum voltage between -3 and -4 v.

A positive bias of 0.6 to 0.8 v is supplied from R_{23} to the anode to provide the required polarization. The switch S_2 changes over from anode-cathode polarization to cathode polarization.

The heaters are supplied from the 22 v secondary via the SV-2 bridge and filter capacitor C_{19} .

The circuit to the cell includes a tapped resistor (input to the amplifier R_{27} to R_{33} , working on S_6 ; R_{23} is present as a first step when anode-cathode polarization is used), the KMS resistance box (R_{24} to R_{26}) and R_{22} , which injects a square pulse of amplitude about 25 mv, which is shaped by the voltage stabilizer T_3 . The capacitor C_{11} in parallel with R_{21} speeds up the flow of charge to the double layer around the drop electrode. I.G. Grinman proposed this circuit detail.

The ac component of the voltage is passed to the input to the three-stage amplifier $T_8\text{--}10$ (which has heavy negative feedback); the output is applied to the right grid of the switching tube T_6 . The two halves of T_6 are connected in a bridge circuit ($\frac{1}{2}6N9 - R_{49} - R_{50} - \frac{1}{2}6N9$). Square pulses are fed to the plates via R_{49} and R_{50} ; T_5 (a thyratron) generates these pulses, and is fed from the 400 v winding via the voltage stabilizers T_4 and T_{11} . The plate pulses are applied 4.3 msec after the start of the positive half-wave in the cell circuit (when the thyratron in the integrating circuit $R_{48}\text{--}C_{22}$ fires); they finish 1 msec before the pulses fed to the cell (the phase-shift network $R_{18}C_9R_{19}C_{10}$ ensures this, since it couples the 400 v winding to T_3).

The mean value of the amplified current passed when the switching circuit is conducting is measured by an M21 reflecting galvanometer (connected to terminals G), which is connected in the measurement diagonal of the bridge; or by a microammeter (M) that reads 100 μ a full scale. The galvanometer is used to extend the range to very low concentrations.

Oscillations caused by the individual drops are filtered out by the $C_{20}R_{45}C_{21}R_{46}$ filter (with the microammeter), or by $R_{55}C_{26}R_{54}C_{25}R_{53}C_{24}R_{52}$ (reflecting galvanometer).

The set-zero controls are R_{62} and R_{61} , which adjust the bias to the left half of the 6N9.

The potentiometers R_{65} and R_{70} set the zero for the galvanometer; they are fed from the 1.5 v battery B. Switch S_8 cuts in this balancing circuit.

The galvanometer is fitted with a four-step Ayrton shunt ($R_{66} - R_{69}$) mounted on switch S_7 ; this shunt is used to vary the sensitivity.

The microammeter can be used as a voltmeter to measure the polarizing voltage. The standard resistor R_{17} ensures that a 20 μ a reading corresponds to 1 v. The zero can be shifted by passing 20 μ a from the plate supply in the amplifier via R_{15} and R_{16} when anode polarizations are to be measured. Switch S_3 (right-hand position) transforms the microammeter to a voltmeter. If the galvanometer is in use, S_3 must be set to the right-hand position, since in this position the filter cuts out; the galvanometer would otherwise be too sluggish.

Switch S_5 (right-hand position) connects the galvanometer (to make ordinary polarographic measurements) across the input resistor (S_6) in the amplifier; this resistor then acts as an Ayrton shunt. The galvanometer can record an ordinary polarogram at the same time as the microammeter records the square-wave polarogram.

The galvanometer is heavily damped (total resistance less than the critical value) to suppress oscillations

during ordinary polarography. Very large oscillations can be suppressed by switching in (with S_4) the capacitor C_{23} and resistance R_{51} . This combination gives the same damping as would a much larger capacitance without R_{51} .

C_{13} and C_{14} filter out high-frequency noise, and stabilize the amplifier.

A metal-braid screen is fitted to the rubber tube that joins the mercury reservoir to the dropping electrode; this screen is connected to the common-earth point of the instrument. The cell is connected via a short-screened lead.

The design is compact, the power comes from a single source, and a panel-mounting microammeter is used; all these features make the instrument useful for routine use in field or factory conditions.

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A NEW CENTRIFUGAL INSTRUMENT FOR SEDIMENTOMETRIC ANALYSES

N.A. Figurovskii and T.B. Gavrilova

(Lomonosov State University, Moscow)

Many modern emulsions and powders have to satisfy two basic requirements (in addition to any special ones), namely that the particle size must be small (in the region of a tenth of a micron) and that the size must show only a small scatter. These demands arise from the need to provide the best possible properties in products in which the materials are used (e.g., in filled rubbers or plastics).

Normal methods of size analysis (sieving, sedimentation, settling in air, microscopic examination, gas flow, etc) cannot provide full curves for the size distribution below one micron. Centrifugal methods have lately come into use again for this reason [1, 2]. The instruments are not very suitable for use with the very fine powders now often used. The centrifugal fields are too large, and the instruments do not give complete and exact size curves.

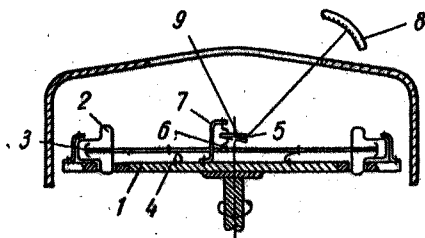


Fig. 1. The centrifuge system: 1) disc; 2) shaped cells; 3) sedimentation cups; 4) springs joining the rod to the disc; 5) moving mirror; 6) springs holding mirror; 7) rod on disc; 8) scale; 9) light source.

Quiet-running centrifuges that give fields in the range from 500 to 3000 g are of great value for use with particles of sizes in the 0.05 to 1 μ range. These machines can readily be fitted with reading devices, such as the photoelectric ones used by Svedberg, MacBain, etc. One of us designed a centrifugal balance in 1948 [3, 4]; the rate of deposition of the material was measured by weighing. The device was not sensitive enough, in spite of some improvements, so we have for some years sought to improve sedimentometric methods.

We describe here a new instrument based on a 1500 rpm centrifuge. The motor is run on a dc supply, to ensure a constant speed; the acceleration is

$$C = \left(\frac{2\pi n}{60} \right)^2 r = 628 \text{ g.}$$