Technical Design of an Oscillopolarograph with a Wide Range of Application

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The conception of an oscillopolarograph is described which can be used for oscillopolarography by applied current of rectangular shape and rectangular or triangular applied voltage. The apparatus renders possible to record single first curves, several subsequent curves and alternating polarization. For work with applied current, the apparatus is provided with incorporated circuits for stabilization of the oscillopolarograms. In respect of design it is constructed as a self-contained polarographic apparatus; for recording of the curves any oscillograph or other recording device can be used.

In our institute the oscillopolarographic method is used for studying proteins, nucleic acids, and their components [1]. Measurements have so far been carried out with the aid of a P 576 Polaroscope designed rather for current technical use. In the interest of further widening and improving the range of application oscillopolarography can find in biology, we have started to tackle the development of a new oscillopolarograph that will enable us to carry out more universal measurements. For the time being, two fundamental oscillopolarographic methods are widely used: oscillographic polarography by applied current [2] and oscillographic polarography by applied voltage [3]. Both methods have been worked out separately, for both methods suitable devices have been developed, some of them possessing universal character [4, 5].

Description of apparatus

When choosing the conception of our apparatus we proceeded from the requirement that both fundamental methods of oscillographic polarography could be employed. The block diagram of the apparatus is shown in Fig. 1. The apparatus itself consists of three basic parts: basic generator, shaping unit and amplifier unit. In the basic generator rectangular pulses are produced with the aid of a multivibrator from which the polarizing waveforms are derived. The pulses are produced within the frequency range of 0.1 c/s to 1 kc/s on frequencies which are multiples of *1* and *5*. The multivibrator is started at any time of the growth of the drop and produces, with the aid of another multivibrator, either *1* pulse or several pulses respectively, or a series of pulses, lasting until the drop is torn off. Thus, we can, in a relatively easy way, produce the first curve or several curves, on a growing surface of the mercury drop, or work with alternating polarization. The detachment of the drop can be controlled within a period of 0.5—10 seconds, or synchronized either with the frequencies of the polarizing waveforms or with their different fractions. In the second case, we thus obtain stabilized oscillograms with one or more curves. The device for the drop-time control used for this purpose is described under reference [6].

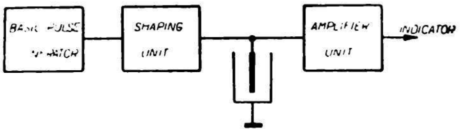

Fig. 1. Block diagram of apparatus.

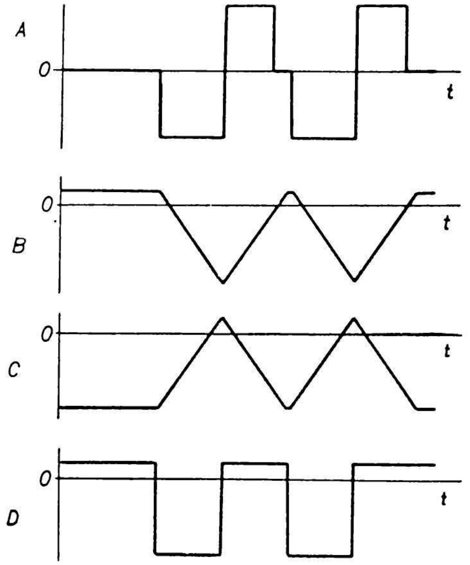

Fig. 2. Polarizing waveforms used in the apparatus.
A. rectangular voltage pulses in applied current oscillographic polarography; *B*. triangular waveforms of applied voltage directed towards negative potentials; *C*. triangular waveforms of applied voltage directed towards positive potentials; *D*. rectangular waveforms of applied voltage.

The shaping unit treats the rectangular pulses from the basic generator and turns them into polarizing waveforms which are applied to the electrodes. In Fig. 2 the polarizing waveforms the apparatus is working with are plotted. In applied current oscillographic polarography the current impulses of rectangular shape are produced by the passage of voltage pulses of ± 100 V amplitude over a sufficiently high resistance into the load. The generated voltage pulses have at the end of their anodic part a certain time-lag on the zero potential (Fig. 2*a*). This time-lag, on the one hand, makes possible to complete the pulses within the required time, on the other hand, it serves for adjusting the D. C. component by shortening or lengthening the anodic part of polarizing waveforms. In applied voltage oscillographic polarography three types of voltage waveforms are used on the whole: the triangular waveform directed towards negative potentials (Fig. 2*b*), the triangular waveform directed towards positive potentials (Fig. 2*c*), and the rectangular one (Fig. 2*d*). By suitable limitation it is possible to produce trapezoidal waveforms from triangular ones. The amplitude of all voltage waveforms can be changed continuously within the range of $+0.5$ V to -2.5 V.

Two D. C. amplifiers serve for amplifying the voltage or current from the polarizing electrode. By means of one of them, derivation of the output signals is carried out according to need. Active derivation with the aid of a D. C. amplifier features great advantages over derivation with the aid of passive RC circuits. The former allows for perfect derivation within the entire frequency range, moreover, it keeps up the signal amplitude or amplifies it as well. The apparatus further provides stabilization of the oscillograms in applied current oscillographic polarography. Constant amplitude of the output oscillograms is reached by maintaining a constant current density on the drop during its growth. For controlling the feedback system, a derivative output signal is being used, the amplitude of which is proportional to the current density on the drop. When the output signal exceeds the set D. C. level, controlling signal is released which is detected and upon amplification controls the level of limitation of the generated polarizing courses and thus their amplitude as well.

The apparatus is designed and constructed as a self-contained polarographic unit. Any oscillograph or any other suitable recording apparatus can be used for recording the curves. The output level of the signals is 100 V, which allows for any magnification of the size of the individual indentations when a standard oscillograph is used.

Experimental

For the sake of illustrating the wide range of application this oscillopolarograph can find we are presenting a few oscillopolarograms of a cytidylic acid solution of 5 . 10^{-4} M concentration in the supporting electrolyte of ammonium formate of 0.3 M concentration with pH 5.6 phosphate buffer, the frequency of the polarizing sweeps being 50 c/s. In Fig. 3*a* is shown the standard oscillographic curve $dE/dt = f(E)$ in applied current oscillopolarography. In Fig. 3*b* there is the same oscillopolarogram stabilized by means of the circuit already described. In Fig. 3*c* the first curve is shown, Fig. 3*d* shows three oscillographic curves of the same solution. In oscillographic polarography by means of applied voltage of triangular shape we obtain analogically similar curves. Fig. 4*a* depicts the standard oscillographic curve $I = f(E)$ and Fig. 4*b* shows the first curve of the same solution.

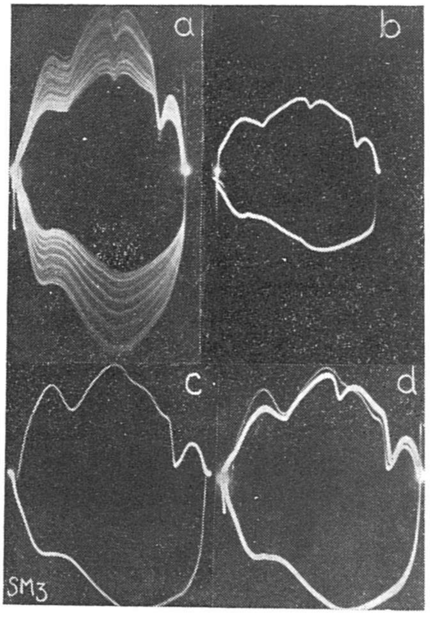

Fig. 3. Oscillographic curves $dE/dt = f(E)$ of cytidylic acid solution of 5 10^{-4} M concentration in supporting electrolyte of ammonium formate with pH 5.6 phosphate buffer in rectangular applied current oscillopolarography at a frequency of 50 c/s.
a) standard oscillogram; *b*) stabilized oscillogram; *c*) first curve; *d*) first three curves.

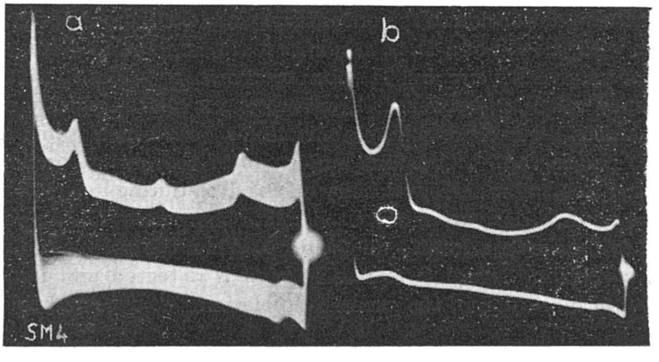

Fig. 4. Oscillographic curves $I = f(E)$ for the same solution in triangular applied voltage oscillographic polarography at frequency of 50 c/s.
a) standard oscillogram; *b*) first curve.

In our paper we wish to point to the possibility of designing and constructing more universal apparatuses that will make possible to apply more oscillopolarographic methods in the research work.

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TECHNICKÝ OPIS OSCILOPOLAROGRAFU S ROZSIAHLOU POUŽITEĽNOSŤOU

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Navrhol sa prístroj na získanie oscilopolarografických kriviek $dE/dt = f(E)$ a $I = f(E)$. Zariadenie umožňuje polarizovať elektródu aj jednotlivými cyklami striedavého prúdu pravouhlého priebehu a striedavého napätia trojuholníkového a pravouhlého priebehu. Stabilizované oscilogramy možno získať polarizáciou kvapkovej elektródy prúdom konštantnej hustoty.

ТЕХНИЧЕСКАЯ СХЕМА ОСЦИЛЛОПОЛЯРОГРАФА С ШИРОКОЙ ОБЛАСТЬЮ ПРИМЕНЕНИЯ

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Была предложена аппаратура для получения осциллополярографических кривых $dE/dt = f(E)$ и $I = f(E)$. Устройство позволяет поляризовать электрод и отдельными циклами переменного тока прямоугольной формы и переменного напряжения треугольной и прямоугольной формы. Можно получить стабилизированные осциллограммы, применяя поляризацию ртутного капельного электрода током постоянной плотности.

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