A SIMPLE METHOD OF DIGITALIZATION OF POLAROGRAPHIC CURVES. DESCRIPTION OF THE APPARATUS*

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The paper deals with the construction of a simple electronic equipment made from commercially available components, suitable for recording alternately the potential and the current data for a polarographic curve on a five-track perforated tape. The apparatus can operate in three modes making it possible either to record the polarographic curve or the current as a function of the time at constant polarization potential or the current-time curves on individual drops.

In evaluating polarographic curves obtained in the form of an analogue record of the current as function of the applied voltage, it is often necessary to obtain a large set of numerical data from graphical records (as in the so-called logarithmic analysis) by means of a ruler. The procedure is not very accurate and moreover rather tedious, hence hardly applicable in the case of a large number of recorded curves. Evaluation of the data by some complicated algorithm leads to additional loss of time.

The problem of the numerical data processing has been simplified in recent years by the application of programmable calculators, however the preparation of the necessary set of data has been a limiting factor. The problem of data collection and processing can be solved by using microprocessors in a single apparatus[1-3], however polarographs with built-in microprocessors are up to now very rate.

Another possibility is the direct connection of a polarograph with a desk calculator as described by Ebel and coworkers[4]. This offers interesting possibilities, the treatment of polarographic data being limited only by the operational speed of the calculator and the size of its memory. The on-line method, however, implies that the calculator serves only the purpose of polarography, a condition which in spite of a broad use of calculators is rather inconvenient.

In the polarographic laboratory of this Institute, the off-line method has been used since 1975 in evaluating the polarographic curves. The potential and current values are recorded on a five-track perforated tape, which is in a further step treated by a desk calculator of the type HP 9830 A using suitable programs. The digitalization equipment designed and constructed by us and its functions are described in the present paper.

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RESULTS

Digitalization Equipment

Since we could not use the d.c. voltage source of the LP 7 type polarograph (Laboratorní přístroje, ČSSR) because of a relatively high noise level causing distortion of the data, we used a d.c. voltage generator of own construction using operational amplifiers. Thus, we obtained d.c. voltage increasing or decreasing linearly with the time at a rate of 0, 20, 100, or 400 mV/min as usual in commercial polarographs, and besides also 5 V/min for a rapid setting of the starting voltage. The voltage ramp was realized by operational amplifiers of the type WSH 220, ensuring a sufficient stability and reproducibility of the potential setting. The voltage ramp generator was provided with an output socket for connection with a pen recorder, and besides with a circuit making it possible to record the polarographic curves with a sensitivity adjustable in seven steps. Another socket enables one to superimpose a stabilized d.c. voltage onto the voltage ramp so as to cause a shift of the potential range exactly by −1·00 V. Thus, it is possible to record curves at potentials more negative than −1·6 V without lowering the sensitivity range of the digital voltmeter MT 100(Metra, Blansko, Czechoslovakia) at −1·60 V. The starting potential of the polarographic curve can be set by using the display of the voltmeter. This shows also the measured quantities during recording the curve in the chosen operating mode. During recording the polarographic curve, the MT 100 voltmeter is switched on to external control and indication. The external indication must be switched off only during setting the voltage ramp to the initial potential. The integration interval of the MT 100 voltmeter was shortened from 40 to 2 ms with regard to the third operating mode described below. This was achieved by a memory circuit connected to the input of the voltmeter.

The output recording unit (Development workshop, Czechoslovak Academy of Sciences, Prague) serves as a signal mediator between the voltmeter and a paper tape punch. All characters were employed except for the "channel" and decimal point. The output punch Consul 332·5 (Závody Jana Švermy, Brno, Czechoslovakia) serves to record the potential values on a five-trakt tape. The minimum time interval between two successive data is 1 s with regard to the performance of the punch.

Two coupled electronic timing relays CR 2·1 and CR 2·2 (Development workshop, Czechoslovak Academy of Sciences, Prague) serve to generate pulses for the drop time control and to initiate the record of the current or voltage. Both these relays consist of two units (Re_1 and Re_2, Re_3 and Re_4) which can be arbitrarily adjusted at 0·01 s intervals. The timing relay CR 2·1 gives the time base for the drop time control in all operating modes, while CR 2·2 derives its function from CR 2·1. The sequence of pilot pulses for the individual operating modes is shown in Fig. 1.

The mode changing switch makes it possible not only to select the operating mode but also to set the drop time control, to select the sensitivity of the measuring circuit

(±16 or ±1·6 V for potential and ±16 or ±160 μA for current), and to synchronize the start of the recording of the *i–t* curve.

The electrolytic cell with the dropping mercury electrode, drop time controller and reference electrode is placed in a Faraday cage to minimize the noise. The voltage ramp generator is also mounted in the cage. The function of the Faraday cage was checked by an oscilloscope. The block diagram of the whole apparatus is shown in Fig. 2, where *A* denotes the polarographic part, *B* the mode changing switch, *C* measuring block, and *D* time base.

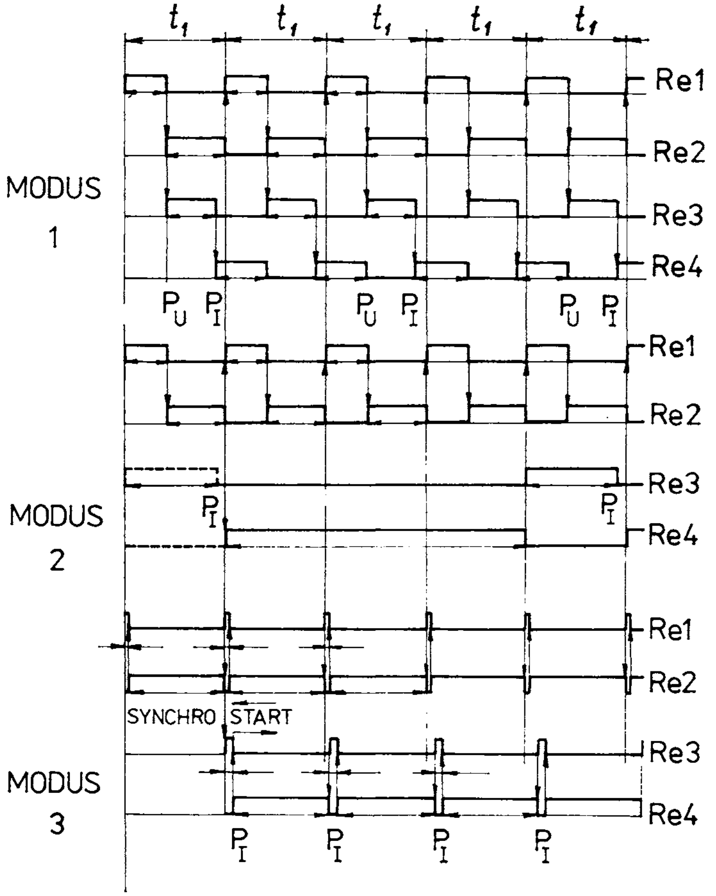

FIG. 1

Time sequence of pulses for different modes of the digitalization apparatus. Mode 1 (record of potential and current): Δt_1 for $P_I = 0{\cdot}2$ s. Mode 2 (record of current as function of time): $\Delta t_1 = 0{\cdot}2$ s for P_I of every fourth (or n-th) drop. Mode 3 (record of *i–t* curve): time increment 0·01 s

Operating Modes

Mode 1 makes it possible alternately to record the applied potential difference between the dropping and reference electrodes and the instantaneous current. It is necessary to choose the drop time, t_1, and the time for starting the pulse for current sampling, P_I, preferably close before the breaking off of the drop. To this end, relay Re_1 is set to $t_1/2 - \Delta t_1$ and relay Re_2 (both on CR 2·1) to $t_1/2 + \Delta t_1$ (*e.g.*, $\Delta t_1 = 0{\cdot}1$ s). Relays Re_3 and Re_4 (on CR 2·2) are set to $t_1/2$. The instant when the current P_I is recorded is exactly in the middle of the time interval between two successive records of voltage P_U. The program for evaluating the perforated tape includes interpolation of the potential records to obtain the potential corresponding to the current record. Further it enables one to correct any experimental errors, *e.g.* due to irregular drop time. A set of interpolated pairs of voltage and current data in a chosen potential range can be obtained from the smoothed curve and treated further in any desired way.

Mode 2 serves to record the current at constant polarization at chosen time intervals longer than t_1. This is suitable for following the chemical reaction rates of polarographically active substances. The data can be used, *e.g.*, to calculate the rate

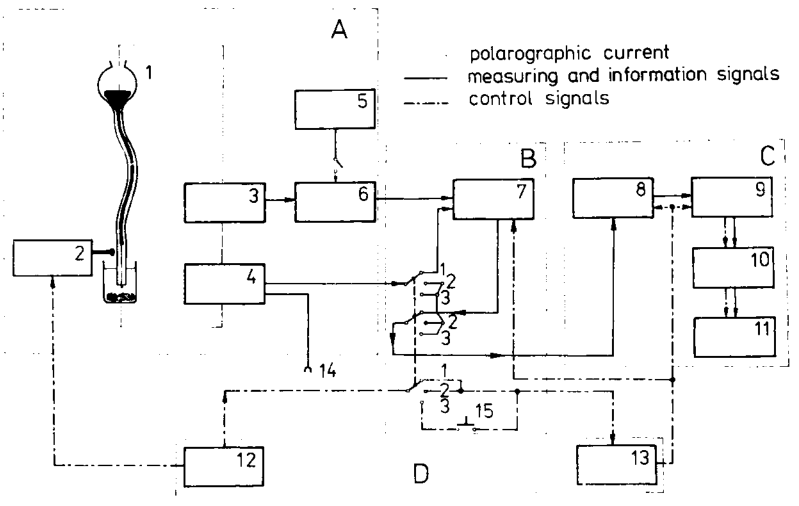

FIG. 2

Block diagram of the digitalization apparatus. **A** polarograph, **B** mode change-over switch, **C** measuring block, **D** time base; **1** dropping mercury electrode, **2** drop time controller, **3** voltage ramp, **4** current-to-voltage converter, **5** external source of superimposed voltage, **6** adder of voltage, **7** voltage-current change-over switch, **8** memory circuit, **9** digital voltmeter MT 100, **10** output recording unit, **11** punch Consul, **12** timing relay CR 2·1, **13** timing relay CR 2·2, **14** output for pen recorder, **15** synchronized start press button constants. To follow the course of a chemical reaction, relays Re_1 and Re_2 (on CR 2·1) are set so that the sum of both values equals the chosen drop time t_1. Relay Re_3 is set to $t_1 - \Delta t_1$ and Re_4 to a whole multiple of t_1 which gives the interval of current sampling during the studied process.

Mode 3 serves to record the values of the instantaneous current density at constant electrode polarization in such a way that the current records on a succession of drops are increasingly more retarded with respect to the beginning of the drop formation. Thus, we obtain a curve which is identical to a current–time curve recorded on a single drop. To this end, both relays on CR 2·1 are set so that the sum of their values equals the drop time t_1. To obtain the highest possible density of points, Re_3 is set to 0·11 s and Re_4 to $t_1 - 0{\cdot}1$ s.

Checking the Operation of the Apparatus

The correct functioning of the apparatus was verified by comparison with reliable data on $E_{1/2}$ values and slope of the waves given in the literature. The first operation mode was tested by recording the linear current–voltage dependence for a constant resistance of 1 MΩ (Ohm's law) in the voltage range from $-1{\cdot}6$ to $+1{\cdot}6$ V (*i.e.* current range from $-1\,600$ to $+1\,600$ nA). The deviations from linearity were only exceptionally higher than 10 nA (*i.e.* 0·6%).

The current–voltage dependence was further verified on polarographic reversible waves for Tl^+, Cd^{2+}, and In^{3+} cations under the conditions given in the literature[5–7]. The values of the half-wave potentials and reciprocal slopes of the waves calculated according to ref.[8] are given in Table I.

For following a chemical reaction polarographically, two examples were chosen and the digital data were compared with the analogue record. Alkaline hydrolysis served as a model reaction, in the first case with DL-α-phthalimidovaleric acid[9] whose reduction wave decreases with the time, in the second case with trifluoroacetamidomalonaldehyde, which hydrolyzes to aminomalonaldehyde, giving an oxidation wave[10]. The rate constant in the first case was the same as in ref.[9] ($0{\cdot}77\ l\,.\,mol^{-1}\,s^{-1}$), in the second it was equal to $4{\cdot}85\,.\,10^{-4}\,s^{-1}$ (ref.[10] gives $5{\cdot}2\,.\,10^{-4}\,s^{-1}$).

For obtaining *i–t* curves of individual drops, cystine[11] in a phosphate buffer of pH 6·8 was chosen as the active compound. The drop time t_1 was maintained at 2·4 s and the time increment of the phase of the measurement was set equal to 0·01 s. Current–time curves at a potential of $-0{\cdot}55$ V (limiting current of the first wave) and $-1{\cdot}20$ V (S.C.E.) (limiting current of the second wave) are shown in Fig. 3.

DISCUSSION

The correct functioning of modes 1 and 2 is substantiated by the data in Table I and in the text (p. 1 118). Deviations of the half-wave potentials from the literature data may be attributed to differences in the content of surface active compounds in the electrolyte. The values of the reciprocal slope are in a fair agreement with those given by Tomeš[12].

The difference in the values of the rate constant for hydrolysis of aminomalonaldehyde is within experimental errors. In calculating the rate constant from the digital record, a substantially higher number of experimental points was used.

The different *i*–*t* curves on the first and second wave of cystine are in agreement with the kinetic-adsorption character of the more positive wave and the diffusion

TABLE I

Test of the first mode — values of $E_{1/2}$ and slopes of the waves for reversible reduction of cations

Cation	Medium	$E_{1/2}$ V (S.C.E.)	$E_{1/2}$ (lit.) V (S.C.E.)	Rec. slope mV	Ref.
Tl^+	0·1M-$NaNO_3$	−0·459	−0·455	−59	5
Cd^{2+}	0·1M-KNO_3	−0·586	−0·578	−32	6
In^{3+}	1.0M-KCl	−0·580	−0·612	−22	7

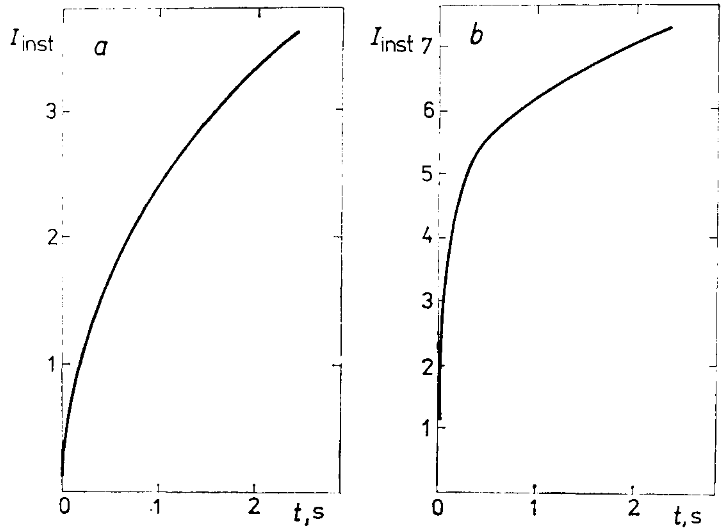

FIG. 3

Current–time curves on successive drops: *a* at −0·55 V (S.C.E.), *b* at −1·20 V. Potential values correspond to limiting currents of the first and second cystine waves (5 . 10^{-4} mol/l, phosphate buffer of pH 6·8). Time increment of the current record 0·01 s, drop time t_1 = 2·4 s (I_{inst} in μA) character of the limiting current of the more negative one. The nonzero value of the current at the beginning of each *i–t* curve is due to the fact that every drop begins to grow starting from a finite size corresponding to the radius of the capillary.

The described digitalization apparatus, constructed from available parts and components in a modular form, enables one rapidly to treat a large ensemble of data. Thus, even complicted reaction mechanisms with the corresponding theoretical equations can be easily verified. Especially the dense sampling of polarographic or kinetic records is advantageous. Another advantage is that errors in potential readings due to inaccuracy of the pen recorder or distortion are eliminated. The third mode enables one to obtain qualitative information about the character of the electrode process from an analogue record of *i–t* curves, which can otherwise be obtained only in a more complicated way.

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