Experimental realization of elimination polarography

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Dedicated to Professor Ľ. Treindl, DrSc., in honour of his 60th birthday

An experimental implementation of elimination polarography based on a previously developed theory is described. For the linear combination of instantaneous polarographic current, its time integral and time derivative, and tasting the resulting function, a DC polarograph adapter was built. The results of capacity current elimination at a micromolar concentration of depolarizers confirm the theory and justify the conclusion that the sensitivity limit is comparable to pulse methods. Moreover, a new effect of current depression before Zn(II) reduction in this concentration range is observed.

В приведенной работе описывается экспериментальное осуществление элиминационной полярографии, основанной на ранее разработанной теории. Для проведения линейной комбинации мгновенного тока, его интеграла и производной, и для тастования конечной функции был построен к полярографу адаптер. Достижения элиминации емкостного тока в области микромолярных концентраций деполяризатора подтверждают теорию и дают возможность сделать заключение о пределе чувствительности сравнимого с пределом детектирования у импульсных полярографических методов. Кроме того, в этой концентрационной области деполяризатора наблюдается новое явление — провал тока перед восстановлением цинка.

Elimination polarography (EP) is a polarographic method comprising the elimination of some particular currents from the total polarographic current by means of a combination of the total current and/or its time derivatives and integrals. The principle and theory of this elimination has been described previously [1]. Generally, it is possible to use derivatives and integrals of any degree.

However, for the sake of experimental simplicity, we have used in the present paper the simple combined function in the form

$$f(i) = a\,i - b\int_0^t i\,\mathrm{d}t \mp c\,\frac{\mathrm{d}i}{\mathrm{d}t} \qquad (1)$$

where i is the instantaneous total polarographic current, t is time starting from the rise of the dropping mercury electrode (DME) and a, b, c are certain coefficients. Generally, these coefficients have to be certain functions of time for the achievement of the requested elimination. However, if the resulting function is tasted only at certain precisely predetermined time, those coefficients are certain constants, the values of which depend on the tasting time chosen. Experimental implementation of linear combination (*1*) with constant coefficients can be simply achieved by means of an analogue technique. This solution has been chosen in the present paper.

The elimination of certain particular currents from the total current is based on the difference of the time dependences of those currents. For a known time dependence the coefficients a, b, c, necessary for the particular current elimination can be theoretically determined. However, it is known that theoretically derived current—time dependences are usually only an approximative idealization, while in fact due to various factors those dependences are more complex [2]. From the elimination theory [1] it follows that elimination can be achieved for any current—time dependence provided this dependence is the same for particular current. Only the values of coefficients for different time dependences are different. It is therefore possible to determine the coefficients experimentally by proper adjustment for selected experimental case. Such coefficients then involve all experimental departures and distorsions of the current—time dependence, including those of instrumental nature. The experimental adjustment of coefficients a, b, and c can therefore be looked at as the special calibration for the elimination of certain component of the polarographic current.

The function used (*1*) contains three terms, and therefore enables the elimination of one or two particular currents. In principle, any particular current can be chosen for its elimination. Some examples, involving elimination of capacity, diffusion and kinetic current, have been demonstrated previously [1], and many others can be proposed. However, in this paper we have examined the possibility of the elimination of the capacity current in the range of low depolarizer concentration.

The elimination of the capacity current in polarography has been the object of investigation of many electrochemists for a long time. A review of this effort was summarized for instance in papers [3—5]. Under the assumption that the polarographic current contains three components, namely capacity (i_c), diffusion (i_d), and kinetic (i_k) current and the simple theoretical power-law current—time dependences hold, the following formulas for the elimination of the capacity current can be used [1].

$$\frac{7}{3}\left(i - \frac{2}{3t}\int_0^t i\,\mathrm{d}t\right) = i_d + \frac{7}{5}i_k \qquad (2)$$

$$\frac{2}{3}\left(i + 3t\frac{\mathrm{d}i}{\mathrm{d}t}\right) = i_\mathrm{d} + 2i_\mathrm{k} \tag{3}$$

These equations form the guide used for experiments described below.

Experimental

Measurements were performed in a three-electrode cell, with a mercury pool as counter electrode, a DME as working electrode and a saturated calomel electrode (SCE) with the Luggin capillary as reference electrode. Mercury flow rate of DME was 0.947 mg s^{-1}, selected drop time was 2 s. All measurements were carried out at laboratory temperature.

Polarograms were recorded with the polarograph OH-105 (Radelkis, Budapest) in connection with an adapter constructed in our laboratory and described below. All measurements of EP were made with maximal sensitivity of polarograph used (3×10^{-10} A per division); for tast polarography the sensitivity 1×10^{-9} A per division was used in order to fit the record scale. A damping 2 was used throughout and scan rate was 0.5 mV per drop time.

The tested solution of Cd(II), Ni(II), and Zn(II) in ammonium buffer was prepared just before starting the measurement by dilution of a stock solution. The stock 1×10^{-2} M solution of Cd(II), Ni(II), and Zn(II) was prepared by dissolving $CdCl_2$, $NiCl_2$, and $ZnCl_2$ in 0.5 M ammonium buffer ($NH_3 + NH_4Cl$) with double-distilled water. All chemicals were of anal. grade and crystalline water of salts used was determined by differential thermal analysis. Oxygen was removed from the solution by bubbling nitrogen. During the experiments the nitrogen was fed over the solution.

The adapter

The general block diagram of a polarographic adapter for performance of EP is shown in Fig. 1. The adapter processes the polarographic current coming as the signal from the polarograph by input *1* and returns the resulting function in the form of a signal back into the polarograph by output *3* for the record of the resulting polarogram. The polarographic current arriving at input *1* is integrated and derived with respect to time by integrator *4* and derivative circuit *6*, respectively. The current, its integral and its derivative are multiplied by coefficients *a, b,* and *c,* adjusted on corresponding potentiometers, and the sum of resulting terms is made by the adder *10*. The sign of the derivative in the resulting sum can be changed by the invertor *7* with the switch *8*. The particular terms of the sum can be switched on/off by the corresponding switches *9*. Since the resulting function should be tasted at a precisely determined time, the adapter contains the internal time base *12*. This time base controls the pulse generator *13*. The pulse from this generator directs the tasting of the created sum by the analogue memory *11*. The result from this analogue memory goes back to the polarograph by the output *3*. The pulse from the generator *13* additionally controls the second pulse generator *14*. The second time pulse resulting from this generator then acts in three ways. Firstly, it causes the hammer *15* to knock the polarographic capillary to start the new mercury drop.

Secondly, it triggers the discharge circuit *5* of integrator in order to start the integration of the polarographic current. And thirdly, it drives through output *16* the stepping motor of the polarograph to make the DME potential step, so that the potential steps for recording the polarogram are synchronized with the drop and during the time of integration of polarographic current the DME potential is constant. The time base permits selection of the drop time in the range from 0.5 to 8 s. Moreover, input *17* for possible use of external time base is provided.

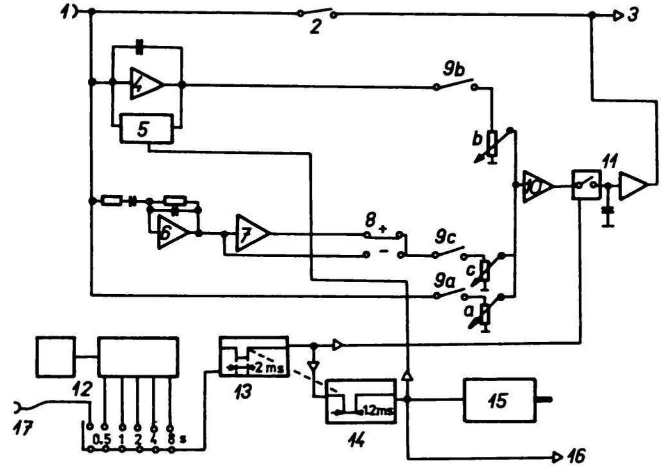

Fig. 1. Block diagram of adapter.
a, b, c — potentiometers for adjustment of corresponding coefficients. *1.* signal input from the polarograph; *2.* shortcut switch; *3.* signal output into the polarograph; *4.* integrator; *5.* discharge circuit; *6.* derivative circuit; *7.* invertor; *8.* switch of invertor; *9a—c.* switches for corresponding functions; *10.* adder; *11.* analogue memory; *12.* internal time base; *13, 14.* pulse generators; *15.* hammer; *16.* pulse output for driving potential step; *17.* input for possible external time base.

The standard connection of all parts, FET IA WSH 220 for integrator, derivative and sampling circuits and IA MAA 741 in other circuits, thermally stable resistances TR 161 and polyester capacitors have been used in constructing the adapter.

The polarograph has been adapted by cutting the input for *y*-axis of polarograph recorder (for polarograph OH 105 Radelkis used the In 5 to plate "L" as described in the block diagram of the manual [6]) and leading the cut ends into the connector of the adapter. The latter device then connects these ends with input *1* and output *3* of the adapter. Moreover, the potential step driving connection in polarograph is cut (connection to input *1* to plate "D" in the block diagram of the manual [6]) and led to the connector for the connection with driving output *16* of the adapter. By using the dummy connector head, connecting the cut leads, instead of the adapter, the polarograph can be used without the adapter as before.

The adapter mentioned was used for all experiments described in the present paper. In the light of experience with its use, further improvements are planned. These involve extension by adding a circuit for the double time integration, adding invertors and switches for the possibility of changing the sign of all terms, adding the pulse generator for possible change of potential step per drop time, and adding a further amplifier to increase the sensitivity with respect to small values of currents.

Adjustment of coefficients

For the elimination of capacity current two possibilities emanating from eqns (*2*) and (*3*) were employed. In the first case, with switches *9a* and *9b* on and switch *9c* off, the potentiometer *a* was set to maximum and compensation was adjusted by the potentiometer *b*. In the second case, with switches *9a* and *9c* on, switch *9b* off and switch *8* at + the potentiometer *a* was set to maximum and the compensation was adjusted by the potentiometer *c*. In both cases the potentiometers used were adjusted in such a way that the EP results at two requested potentials of DME (−1.0 V and −1.1 V in our experiment) were equal.

Results and discussion

The resulting elimination polarograms are shown in Fig. 2, the curve *A* for the integration elimination and the curve *B* for the derivative elimination of the capacity current (corresponding to eqns (*2*) and (*3*), respectively). Described EP

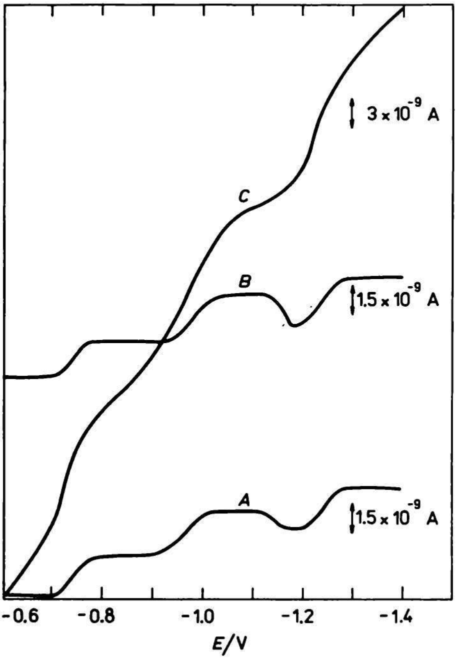

Fig. 2. Elimination and tast polarograms. Polarograms of 2×10^{-6} M solution of Cd(II), Ni(II) and 1×10^{-6} M solution of Zn(II) (0.5 M ammonium buffer (NH_3 + + NH_4Cl), pH = 9.5). *A*, *B* — the polarographic curves with the elimination of capacity current by integration and derivative, respectively, *C* — the tast polarographic curve.

using analogue technique and tasting can in the case of capacity current elimination also be considered as a tast polarography with internal elimination of capacity current. The comparison with the tast polarography results can therefore well exhibit the power of the EP. The tast polarogram of the same solution is therefore given in Fig. 2 along with as the curve *C*.

It can be seen that the tast polarography in accordance with generally stated analytical sensitivity limits [4] cannot give meaningful information in the concentration range used, while EP enables accurate measurement of the depolarizer concentration. The instrumentation used did not allow determination of the sensitivity limit of EP because of insufficient current amplification. However, from the present results it can be deduced that this limit is at least by one order of magnitude lower than the concentration range used. It can therefore well cope with the sensitivity limits stated for pulse methods [4].

Present results confirm the correctness of the conclusion about the possibility of complete elimination of different polarographic currents [1]. The correctness of the conclusion that the coefficients adjusted for elimination of a particular current can be applied generally as long as the current time dependence (including instrumental distortion) is the same was also confirmed. Coefficients once adjusted apply with given adjustment of other instrumental parts to any measurement with the capacity current elimination.

The elimination polarograms exhibit, moreover, one interesting phenomenon — the depression of current before the reduction of Zn(II) at the potential -1.2 V (Fig. 2). It was found that this depression can be observed only at low depolarizer concentrations. Due to this fact, this effect has not, as far as we know, been observed and reported to date, and EP allowed it to be discovered. The difference in the shape of this depression on both dependences used for capacity current elimination (curve *A vs. B*) indicated a complex current—time dependence involved in this effect. However, a detailed study of the nature of this effect will be the subject of a future work.

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