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*Controlled-Growth Drop Mercury Electrode**

Kroplowa elektroda rtęciowa o kontrolowanym wypływie rtęci**

The basic feature of the conventional dropping mercury electrode (DME) are the periodically renewed mercury surface and complete regeneration of the solution in contact with electrode. These features enable the registration of reproducible current-voltage curves and their use without further investigation for analytical purpose or, with further treatment, for kinetic study of reactions taking place in the polarographic electrolysis. Another experimental approach utilizing a single mercury drop which offers information on the type of the electrode process involved is to record the variation of the current with time during the life of a single drop. The shapes of these curves allow to distinguish some kinetic currents, and to demonstrate the presence of adsorption phenomena.

Utilization of a single mercury drop, growing spontaneously (DME), involves a few experimentally unremovable effects:

i. The instantaneous current with the first drop is larger than that registered with the second drop, especially at the beginning of the drop time,

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ii. Low faradaic to charging current ratio at the beginning of the drop time, is responsible for the deviation from the parabolic shape of the current-time curves.

For some time now since the electro-mechanically controlled Hg drop (SMDE) began to be applied in electrochemistry [1,2] some authors have tried to utilize such fast growing drop for area step experiments [3].

However, (distinct) hydrodynamic effects appear when the mercury drop is growing in a very fast mode disturbing the currents observed on the drop growth period. Therefore only a quiet expansion of the mercury drop gives the relationship which offers information on the electrode process.

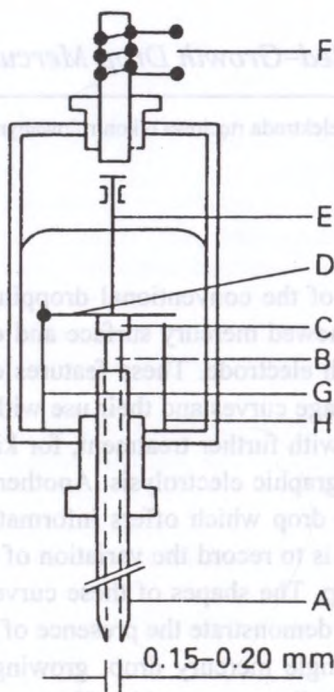


Fig. 1. Diagram of the CGMDE assembly. (A) Capillary; (B) metallic tube; (C) rubber gasket; (D) flat spring; (E) pulling rod; (F) selenoid; (G) spacer and (H) support (Kowalski [5])

The approach offered by the controlled-growth mercury drop electrode (CGMDE) [4,5] combines the advantages of both the conventional DME and the SMDE. In this electrode the mercury outflow (drop growth) is controlled by

a fast response valve, actuated by a pulse sequence generated by a pulse sequencer or a computer, which causes the drop size to increase in step by step mode. The drop size can be described operationally by specifying the number of pulses at the given pulse width. Hence the velocity of the growth of the drop can be controlled by the time intervals between the pulses operating the valve.

The operation of the electrode consists in the flow of mercury out of the reservoir through a capillary of the large internal diameter (0.1–0.3 mm). The capillary has a metallic tube in its upper part. This tube, a flat spring and a washer comprise a fast operating valve. The valve is activated by means of a pulling rod and a solenoid.

The dynamics of the step by step growth of the drop depends on the time intervals between the pulses operating the valve. Hence, in an extreme example, when the valve is energized by one long pulse the drop is generated in one step as with the SMDE described by other workers [1,2].

There are several advantages expected from the principles on which the device is based. (i) The drop mode of growth, rate and drop size can be modified by the pulse sequence and programmed in advance; (ii) sampling of the current can be made during the off-pulse time; (iii) recalibration of the drop size should be easy and could be achieved automatically by generating the drop with a pulse sequence until it reaches a gravity-controlled size.

Some of the above features make the polarographic detector an integral part of the measuring system. The limitations include the mechanical cutting-off of the mercury outflow and the step-like movement of the drop which may produce some vibration of the drop. However, these possible limitations can be reduced if the technical problems are solved.

The above mode of drop generation implies the possibility of current sampling in the OFF pulse time of the pulse sequence which generates the drop. If this sampling is done with a delay long enough with respect to the cell time constant, the sampled current will have very low charging component.

As Figure 2 shows, the individual drop is generated by a package of pulses "a" and (hence) the response is transmitted in the form of a sequence of current samples Q "b". Accordingly, the values of the sequence of these current samples represent the dependence of the current upon time on a single drop and reproduce very well the features of the instantaneous current (i - t curves) of a continuously growing single drop.

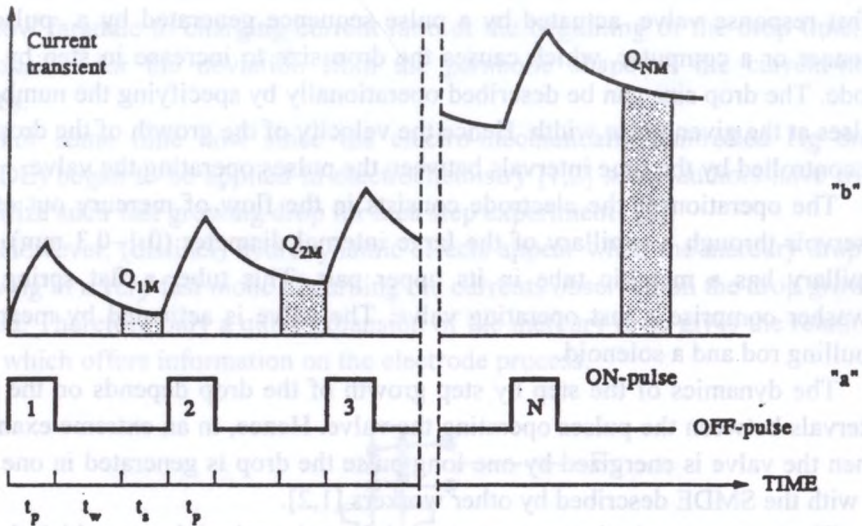


Fig. 2. Schematic procedure for recording the current-time profile using CGMDE. Pulse sequence generating the Hg drop in a step-by-step mode "a", and the resulting current-time profile "b" (Kowalski and Migdalski [6])

The shape of these quantized curves makes it possible to distinguish some kinetic currents, and may indicate the presence of adsorption phenomena.

Each sequence of current samples generated by a package of pulses and processed in the computer gives a single number which represents the shape of the $i-t$ curve.

A constant value of such shape parameters is the evidence of the standard conditions under which the concentration measurement is done. The most frequent case which questions the credibility of the measurements is the sudden appearance of s.a.s. (surface active substance) or a sudden change in its concentration.

Because only at the later stage of the drop life time the current deviates most visibly from the diffusion-controlled value when s.a.s. is present in the solution, the shape parameter can be a supplementary warning about this undesirable effect. When having a set of polarograms it is possible to choose the most reliable of them.

If the proposed procedure should be applied in practice, it would be necessary to show how far the exponents of parabola (shape parameter) are constant for different concentrations of the depolarizer. An experiment carried out with

cadmium confirmed this. Table 1 presents the exponents of parabola b , for $i-t$ curves of cadmium determined from the last 3,4,5,6, or 7 current samples for two different concentrations. The concentrations differ from each other almost by 10 times. The next example shows how far the shape parameter can be helpful to detect the appearance of s.a.s. in the solution.

Table 1. Exponents of parabola (shape parameters) presented for final fraction of the drop life time (Kowalski and Migdalski [7]).

Exponent of parabola	1) 0.5 mM Cd.(II), 0.5 KNO ₃	2) 0.06 mM Cd.(II), 0.5 KNO ₃
b(3)	0.22	0.24
b(4)	0.24	0.24
b(5)	0.26	0.26
b(6)	0.31	0.31
b(7)	0.36	0.34

The change in the shape of this curve under the influence of s.a.s. has been determined in this case through the analysis of the initial period of the drop life (first seven steps) and of the final fraction generated in the last thirteen steps. Table 2 presents experimental data taken from $i-t$ curves for cadmium. Current samples were taken with 150 ms delay after the drop growth was stopped. In these experiments the starting conditions were determined by pure 1 M KNO₃ as the supporting electrolyte. To demonstrate the adsorption phenomena on the $i-t$ curve recorded in this way, different amounts of Triton-X were added to the starting solution. The numbers listed in Table 2 (in the first and third columns) reflect the shapes of the $i-t$ curve recorded:

- i) within the first 7 steps, and
- ii) within the last 13 steps.

The current samples in columns 2 and 4 were read after the 7th and the 20th steps.

These results confirm the already existing observations in this matter that in the later period of the drop life the current deviates more significantly from the diffusion controlled value than in the earlier period of the drop life. The decrease in the exponent value is significant (numbers in brackets represent the percentage changes with respect to pure solution).

The results listed in the columns 2 and 4 illustrate how far the limiting current has decreased. The correlation between columns 1,2 and 3,4 is obvious.

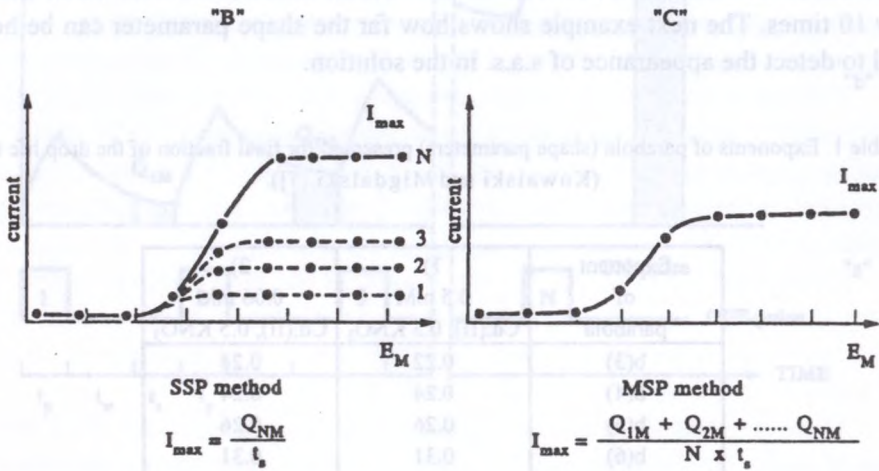


Fig. 3. Schematic procedure for recording the multiple sampling polarogram (MSP) using CGMDE electrode in the Computer Aided Experiment (CAE) and for the staircase technique; "B" — the set of the "Single Sampling Polarograms" (SSP) obtained at successive controlled drop areas (in practice the solid line profile "N" is recorded); "C" the profile of the "Multiple Sampling Polarogram" (MSP), (Kowalski and Migdalski [6])

There is still another feature, a very essential one, regarding the possibility of increasing the accuracy of measurement, also resulting from the way the drop is generated. When the current is sampled after each step of the drop growth, and after all current samples are summed up a high value of the current is obtained when compared with the single sampling procedure at the end of the drop life. In this method the sampled currents after summation supply a very reproducible signal of large size.

This variant has been named by us a "Multiple Sampling Polarography" (MSP). The principle of this method is illustrated in Figure 3. As we can see, during the generation of an individual Hg drop by a pulse sequence the charge is measured after each increment of the drop size. The measured charge samples, corresponding to the given value of the polarizing voltage are next summed up, recalculated per sampling time unit and the obtained current values are displayed in the form of a MSP polarogram. The number of charge samples to be summed up may be programmed in advance up to $(N_{\max} - 1)$, where N_{\max} indi-

icates the number of pulses required to generate a gravity controlled Hg drop and it is determined during electrode calibration. It can be seen from Figure 3(b) and 3(c) that the current values in the MSP method are always lower when compared with single sampling registration. For a given value of the polarizing voltage (E_M) the current value measured by the MSP method is equal to:

$$I_{\max} = \frac{Q_{1M} + Q_{2M} + \dots + Q_{NM}}{N_{xt}}, \quad (1)$$

whereas for the single sampling registration we get:

$$I_{\max} = \frac{Q_{NM}}{t}. \quad (2)$$

Table 2. Effect of Triton-X on the shape of the i - t curve and the diffusion controlled current in cadmium solution (0.2 mM) (Kowalski and Migdalski [7])

Exponent	i_7	Exponent	i_{20}	Triton-X
0.20	0.63	0.30	0.88	0
0.19	0.62	0.26	0.84	$2 \times 10^{-4}\%$
0.19 ₍₅₎	0.60 _(4.7)	0.24 ₍₂₀₎	0.78 ₍₁₁₎	$3 \times 10^{-4}\%$
0.18 ₍₁₀₎	0.50 ₍₂₀₎	0.15 ₍₅₀₎	0.22 ₍₇₅₎	$6 \times 10^{-4}\%$

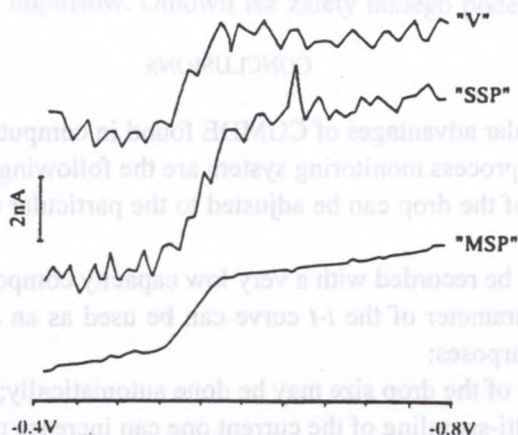


Fig. 4. Comparison of the "noise level", voltamperogram (V) and Single Sampling Polarogram (MPS). The Hg drops were of the same size, generated by N corresponding to 10 pulses, with ON-pulse time 5 ms N_{\max} corresponding to 33 for a gravity-controlled Hg drop. Staircase technique, solution $2 \mu\text{M Cd(II)}$ in 0.1 KNO_3 (Kowalski and Migdalski [6])

The method of polarograms registration with single current sampling after completion of the generation of the Hg drop has been named here "Single Sampling Polarography" (SSP). One can see, as exemplified by staircase polarography, how far it is possible to improve the quality of the registered dependences using the MSP method. The discussed advantages can be estimated by a comparative method when realizing in succession the measurements using: voltametric method (V), single sampling polarography method (SSP), and multiple sampling polarography method (MSP). Figure 4 presents the voltamogram and polarograms registered for 2 mM Cd(II) solution using the staircase technique. The cadmium ion concentration was chosen close to the detection limit for the staircase technique. In each case the Hg drop was generated by a sequence of 10 pulses. When the multiple sampling polarogram was recorded, in the course of each Hg drop generation 10 charge samples were accordingly measured and summed up.

A comparison of the staircase profiles from Figure 4 shows how far the "MSP" method reduces the levels of perturbations. It seems that the application of this method allows the limit of detection to be decreased. The voltamogram "V" and the polarogram "SSP" were disturbed here in a similar degree. This is evidence that the observed perturbations are due rather to external factors (for example, vibration of the laboratory table) and are not to be connected with the Hg drop generation step (it should be remembered that the voltamperogram was recorded on a single Hg drop, generated before the measurements started).

CONCLUSIONS

The particular advantages of CGMDE found in computer aided experiments important for a process monitoring system are the following:

- parameters of the drop can be adjusted to the particular electrochemical conditions;
- $i-t$ curve can be recorded with a very low capacity component;
- the shape parameter of the $i-t$ curve can be used as an additional parameter for analytical purposes;
- recalibration of the drop size may be done automatically;
- by using multi-sampling of the current one can increase the S/N ratio.

REFERENCES

- [1] Peterson M.W., *Am.Lab.*, 69 (1979) 11.
- [2] Novotny L., [in:] *Proceedings of the J.Heyrovsky Memorial Congress on Polarography*, August 25–29, Prague 1980, II, 129.
- [3] Bond A.M., Jones R.W., *Anal.Chim.Acta*, 121 (1980) 1.
- [4] Kowalski Z., Wong K.K., Osteryoung R.A., *Anal.Chem.*, 59 (1987) 2216.
- [5] Kowalski Z., *Analyst*, 113 (1988) 15.
- [6] Kowalski Z., Migdalski J., *Talanta*, 41, 2(1994) 309.
- [7] Kowalski Z., Migdalski J., *Contemporary Electroanalytical Chemistry*, Plenum Press, New York 1990.

STRESZCZENIE

Kropłowa elektroda rtęciowa wyróżnia się licznymi zaletami wynikającymi zarówno z właściwości rtęci jako materiału elektrodowego, jak i odtwarzalności kolejnych kropli w czasie wypływu rtęci z kapilar o różnych przekrojach.

Konwencjonalna metoda wytwarzania elektrody kropłowej, z uwagi na jej liczne wady, a przede wszystkim na sposób jej obsługi, została praktycznie zastąpiona innymi, umożliwiającymi zdalne sterowanie wypływu rtęci z kapilar.

Autor, nawiązując do cech metrologicznych znanych metod generowania kropłowej elektrody, poświęcił uwagę głównie wytwarzaniu kropłowej elektrody rtęciowej ciągiem impulsów. Omówił też zalety takiego podejścia ze względu na elektroanalizę.

