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INCREASING THE SIGNAL TO NOISE RATIO IN AMPEROMETRY AND POLAROGRAPHY USING THE CONTROLLED-GROWTH MERCURY DROP ELECTRODE

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Summary—A new approach to current sampling in amperometric and polarographic measurement is described. This approach requires the application of a step-by-step mode of mercury drop generation. The advantages are: (1) in amperometric measurements an increase of the signal to noise ratio; (2) in polarographic measurements and computer aided experiments the noise level can be markedly reduced.

For some time now a number of papers have been published referring to the various aspects of the mechanical generation of the mercury drop as an electrode to be used for electroanalytical purposes.

The hanging mercury drop electrode (HMDE) is suspended at the end of the mercury thread in a capillary of 0.1–0.3 mm internal diameter and is produced by the movement of a piston. The size of the drop is controlled by a microscrew which moves the piston.

The description of such a device and its application was published more than 35 years ago,[1] followed by numerous modifications of the HMDE.

The principle of the static mercury drop electrode (SMDE) consists in mercury flow through a glass capillary. The outflow of the mercury is forced by gas overpressure,[2] or by the hydrostatic pressure of the mercury column.[3,4,5] The capillary has a diameter of 0.15–0.30 mm, similar to that of HMDE. Here the electrode assembly incorporates a valve which allows the mercury flow to be stopped at selected time intervals to produce a stationary drop.

The most attractive characteristic of the SMDE, as emphasized by the authors and the producers of the device, is obviously the possibility of remote control of the valve and this feature attracted the attention of the users.

It should be remembered that the conventional dropping mercury electrode assembly, DME, generates mercury drops periodically. A spontaneous outflow of mercury from the capillary occurs under the hydrostatic pressure of the Hg column, and the life time of the gravity controlled drop (usually 1–10 sec) depends on the internal diameter of the capillary. A relatively long drop life time of the Hg drop (for SMDE the drop life time is only 50–200 msec) allows for utilization of *i–t* curves.

The approach offered by the Controlled Growth Mercury Drop Electrode, (CGMDE)[6,7] by its principle offers additional sophisticated experimental possibilities. 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 by a computer, which causes the drop size to increase in a 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. It should be noted here, that the valve may be actuated even by pulses of 1 msec duration. In this case, the valve must be usually actuated several hundreds of times to obtain the size of a gravity controlled Hg drop.

Such a method of the drop generation in a quantized way makes possible recalibration of the system and opens new possibilities of its practical application.[8] The general properties of a CGMDE electrode,[6,8] with consideration given to the possibilities of its application in industry[9] have been described in earlier studies. In the present paper the authors demonstrate to

Table 1. Size and quality of amperometric signals as a function of waiting time for two different variants of Hg drop generation—CGMDE and SMDE; 10 μM Cd(II) in $0.1N$ KNO_3, electrode held at -0.65 V *vs* Ag/AgCl

	CGMDE*		SMDE†	
Waiting time t_w (*msec*)	Mean current (*nA*)	SD (%)	Mean current (*nA*)	SD (%)
20	489.2	0.29	1082.6	4.60
40	397,4	0.42	760.2	8.10
60	314.5	0.27	545.2	11.00
120	175.0	0.60	318.6	2.80
220	104.0	0.68	254.0	4.60
420	94.4	0.89	185.4	1.90
1020	83.7	0.81	129.6	0.98

*Hg drops generated by 30 pulses, 4 msec. ON-pulse time, 200 msec OFF-pulse time.

†Hg drops generated by 1 pulse, 270 msec. ON-pulse time.

what extent the employed mode of Hg drop generation eliminates the "long term noise" in amperometric measurements and increases the S/N ratio in polarographic and voltammetric measurements.

EXPERIMENTAL

All chemicals were analytical grade and were used without further purification. All solutions were deareated with purified argon gas for 30 min or longer before each experiment. All measurements were carried out using home-made Controlled-Growth Mercury Drop Electrode (CGMDE) as described in[7] and a microprocessor based electrochemical analyser PP-07 (constructed in our Department of Analytical Chemistry).

RESULTS AND DISCUSSION

In polarographic or voltammetric practice when the SMDE drop is produced in one step, a long waiting time is required for a newly formed Hg drop to be quiescent before any current measurement. A wrong choice of the waiting time results in precision errors.

The presentation of the advantages in this respect of the Hg drop generation in the step-by-step mode (CGMDE variant) is illustrated by the data collected in Table 1.

In this experiment an electrode device containing a capillary with the internal diameter of about 0.1 mm was used, which involved generation of the gravity controlled Hg drops (Hg drop with the maximal size) by 47 pulses, 4 msec. ON-pulse time each. The results of amperometric measurements performed on Hg drops generated in SMDE and CGMDE variants are presented in columns 2 and 4.

The waiting time, (indicated as t_w), preceeding the current sampling was counted since the moment the Hg drop generation had been completed and it was varied in the range 20–1000 msec. It should be noted that the final sizes of the Hg drops generated in the SMDE and CGMDE variants were identical.

The standard deviations, calculated on the basis of 10 successive current readings, performed on 10 subsequently generated Hg drops are given in columns 3 and 5.

As it can be seen from the results listed in column 5, for a SMDE variant the current measured after the waiting time of 20 msec demonstrates a high dispersion of the results. After the waiting time had been extended to 1000 msec a considerable improvement in the repeatability could be observed, but at the same time the current signal decayed almost 10 times.

When a Hg drop is being generated by the step-by-step mode (CGMDE variant), then, already after a 20 msec waiting time the measured current is minimally disturbed (SD = 0.29%). The advantages of the step-by-step mode of the Hg drop generation are illustrated in a different way in Figs 1(a), (b) and (c), which show current values in the amperometric experiments, recorded on 30 subsequently generated Hg drops. The final sizes of the Hg drops generated in SMDE and CGMDE variants were here also identical and the generation parameters were the same as for Table 1.

As it follows from Fig. 1(a) for a waiting time equal to 60 msec the dispersion of the results is very high for the SMDE variant. On the contrary, for the CGMDE variant and the same waiting time the dispersion is minimal and the measured current is only two times lower in comparison with SMDE variant.

Yet, when the waiting times are as long as 1 sec or 2 sec, the repeatability of the current measured for both: SMDE and CGMDE variants is comparable and relatively good (Figs 1(b) and (c).

The optimal waiting time for a Hg drop generated in the CGMDE variant appears to be equal to 60 msec, however, according to the standard deviation values found in Table 1, column 3, this parameter may be reduced here even to 20 msec without loss of precision (SD < 1%).

Accordingly to obtain current samples with the standard deviation value less than 1%, the

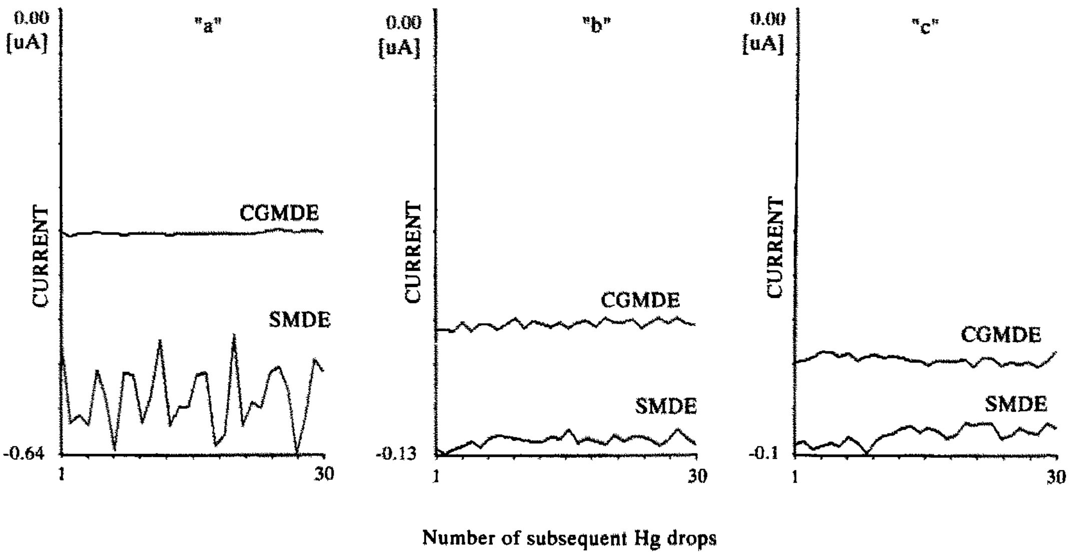

Fig. 1. Size and reproducibility of amperometric signals for two different variants of Hg drop generation—SMDE and CGMDE. Each curve shows 30 current readings carried out on subsequent Hg drops. Parameters of Hg drop generation: SMDE—1 pulse, ON-pulse time 270 msec, CGMDE—30 pulses, ON-pulse time 4 msec, OFF-pulse time 200 msec. Waiting time preceeding current sampling; (a) 60 msec, (b) 1000 msec, (c) 2000 msec; 10 μM Cd(II) in $0.1N$ KNO_3, electrode held at -0.65 V *vs* Ag/AgCl.

waiting time should be longer then 1 sec for Hg drops generated in the SMDE variant. The current value in this case is about four times smaller in comparison with those for the CGMDE variant and the waiting time equal to 20 msec.

In both discussed variants of the Hg drop generation the over extension of the waiting time did not bring about any improvement of the repeatability, which is demonstrated in Fig. 1(b), (c). It appears that the results are even worse for the waiting time equal to 2 sec—this can be seen as a long term drift, especially for the SMDE variant. In such conditions the susceptibility for deformation of the "developed" diffusion layer is probably responsible for this effect.

A similar experiment as described above was performed using electrode device containing capillary with an internal diameter of about 0.25 mm which involves faster mercury flow rate when the valve is open. Gravity controlled Hg drops (Hg drop of maximal size) were generated here by 23 pulses, 2 msec ON-pulse time each. This means, that the growing time of a maximal size Hg drop (*i.e.* 23 pulses × 2 msec ON-pulse time = 46 msec) was four times shorter in comparison with the 0.1 mm internal diameter capillary.

The obtained relations between the size of the current values and their precision in regard to waiting time were similar to those collected in Table 1. It should be noted that Hg drops in both generation variants had also the same size and were generated by 10 pulses, 2 msec ON-pulse time each with OFF-pulse time equal to 200 msec in the CGMDE variant or by a single pulse as long as 53 msec in the SMDE variant.

The above results indicate a major increase of the signal precision and its size if current sampling is done just after completion of the Hg drop generation in the CGMDE variant.

The generation time of the Hg drop in the CGMDE variant is always longer than that for the SMDE variant since the individual growing steps are divided by the OFF-pulse times. For example, the generation time of the Hg drop was equal to 2020 msec in the CGMDE variant and to 53 msec in the SMDE variant (at a capillary of 0.25 mm internal diameter). Because the generation time is often one of the factors determining the maximal frequency of amperometric measurement, we decided to estimate the time interval elapsed from the start of the Hg drop generation to the start of the current sampling for both variants of Hg drop generation, and named it the slice time, t_{slc}. The slice time is equal to:

$$t_{slc} = t_{generation} + t_w$$

Table 2. Size and quality of the current samples for three selected values of the "slice time" (t_{slc}, period of the time elapsed from the start of drop generation to the start of current sampling) and two different variants of Hg drop generation—CGMDE and SMDE. Details in the text; 60 μM Cd(II) in 0.1N KNO_3, electrode held at −0.65 V *vs* Ag/AgCl

t_{slc} (*msec*)	2040		1040		540	
Variant of Hg drop generation	CGMDE	SMDE	CGMDE	SMDE	CGMDE	SMDE
$\bar{I}$ (μA)	5.093	0.631	6.561	0.860	7.139	1.171
SD (%)	0.73	0.82	0.43	0.85	0.84	1.39

and is described for both variants by the equations:

$$t_{slc.CGMDE} = n\,[t_{ON\text{-}pulse\ CGMDE} + t_{OFF\text{-}pulse\ CGMDE}] + t_{w\ CGMDE}$$

or

$$t_{slc.SMDE} = t_{ON\text{-}pulse\ SMDE} + t_{w\ SMDE}.$$

In our experiments the same values of the slice time were used in both variants of Hg drop generation and were obtained by adjusting $t_{OFF\text{-}pulse\ CGMDE}$ and $t_{w\ SMDE}$ parameters.

The other parameters were constant and equal to: $n = 10$, $t_{ON\text{-}pulse\ CGMDE} = 2$ msec, $t_{w\ CGMDE} =$ 20 msec for CGMDE variant, and $t_{ON\text{-}pulse\ SMDE} =$ 53 msec for SMDE variant. It is clear now that for the same slice time

$$t_{w\ CGMDE} \ll t_{w\ SMDE}$$

In the further experiment it was tested how far the slice time may be shortened for both variants of the Hg drop generation without loss of precision, *i.e.* how long the standard deviation values are less than 1%. The Table 2 lists the results of amperometric measurements performed for 60 μM Cd(II) in 0.1N KNO_3 and for three different values of the slice time, illustrating the precision and the size of the current samples with respect to the slice time for both variants of Hg drop generation. As it can be seen, the current values measured for the slice time equal to 1040 msec are almost eight times greater for the CGMDE variant, and at the same time, the standard deviation values are two times smaller in comparison with those of the SMDE variant.

The observed differences in the precision of the current sampling for both variants of Hg drop generation may be due to different factors, for example by the Hg drop and the whole electrode device vibration or by the hydrodynamics effects accompanying the fast growing drop. To explain which effect prevails, the shapes of the charging current and the Faradaic current were recorded. The record was started at

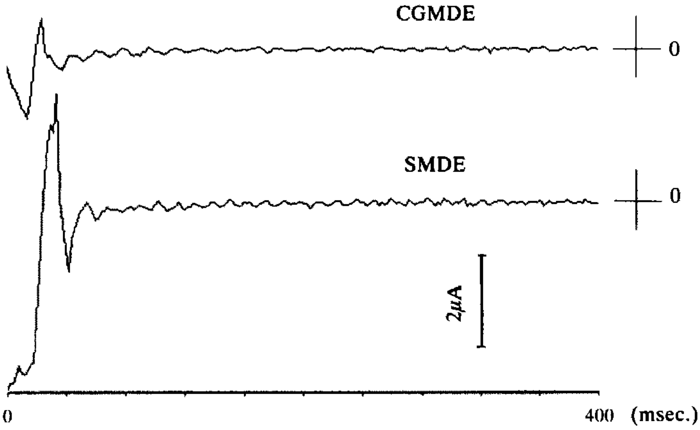

Fig. 2. Profiles of the charging current for SMDE and CGMDE variants. Recording was started at the moment the Hg drop generation was completed. Parameters of Hg drop generation: CGMDE—10 pulses, ON-pulse time 2 msec, OFF-pulse time 200 msec; SMDE—1 pulse, ON-pulse time 53 msec; 0.1N KNO_3, electrode held at −0.65 V *vs* Ag/AgCl.

the moment the generation of the Hg drop had been completed. The profiles of the charging current, recorded for $0.1N$ KNO_3, are shown in Fig. 2. Ringing of the charging current, we believe is brought about by reshaping of the Hg drop after the valve has been closed (causing the double layer deformation), this can be seen in both variants of the Hg drop generation, *i.e.* SMDE and CGMDE (see Fig. 2), and as we observed the ringing time and its amplitude are reproducible. The magnitude of this effect is about three times higher for SMDE variant and the vibration persist longer. The Faradaic current profiles were recorded for 0.7 mM Cd(II) in $0.1N$ KNO_3 using the SMDE and CGMDE variants of mercury drop generation. Figure 3 shows five Faradaic current profiles for each variant, recorded on five subsequently generated Hg drops. An excellent reproducibility of the recorded profiles can be observed only for the CGMDE variant. In the SMDE variant an instantaneous increase of the Hg drop size causes such considerable convective perturbations of the diffusion layer, that the resulting current values are larger than those predicted by the Cottrel equation and vary unreproducible, which is seen on the subsequently recorded current–time profiles. Taking into account the current scale in Fig. 3 and comparing it with that in Fig. 2 it can be seen that the double layer perturbations cannot be responsible for poor reproducibility of the Faradaic current observed in the SMDE version.

Lower reproducibility of the "area-step" experiment with application of the SMDE type electrode has been also reported earlier by Anderson.[10]

Since in the CGMDE variant an individual Hg drop is generated by a package of pulses, the response is transmitted in the form of a sequence of current samples. Summing up such current samples, measured during individual Hg drop generation, seems to be a good way to improve the quality of the registered polarograms and has been proposed by us earlier as "multisampling variant".[9] It has been shown earlier that the vibration of the Hg drop, *i.e.* the "ringing effect" (causing the main fluctuation of the charging current) decays very quickly here. In this way the current measured after a lapse of some tens of milliseconds within the "OFF-pulse time" is free from the capacity component (this time ranging from 10 to 50 msec depending on the internal diameter of the capillary). Because the mean current values are calculated in our electrochemical analyser from the charge measured during the sampling time, two modes of polarographic measurements in the "multisampling variant" can be realized in practice.

(1) The charge samples measured after each Hg drop size increment are immediately recalculated to the mean current values, and next these values are summed up. This mode of "multisampling" measurement was used by the authors earlier.[9]

(2) Charge samples measured after each Hg drop size increment are summed up, whereas the mean current value is recalculated after the Hg drop generation has been completed.

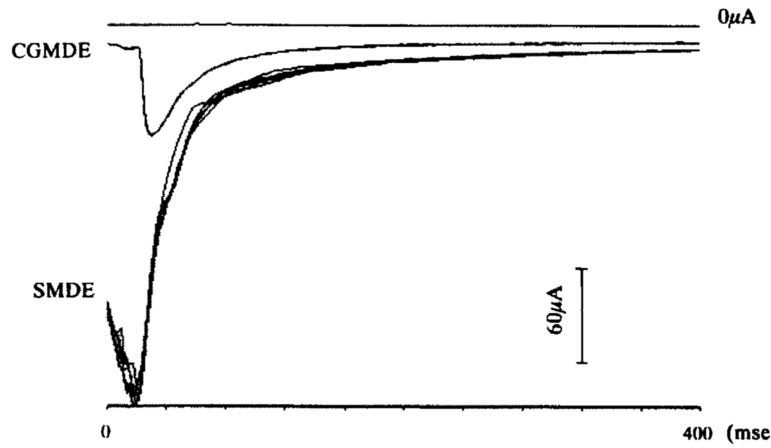

Fig. 3. Reproducibility of the Faradaic current profiles recorded on 5 Hg drops subsequently generated in the SMDE and CGMDE variants. Each recording was started at the moment the Hg drop generation was completed. The parameters of Hg drop generation are the same as for Fig. 2; 0.7 mM Cd(II) in $0.1N$ KNO_3, electrode held at -0.65 V *vs* Ag/AgCl.

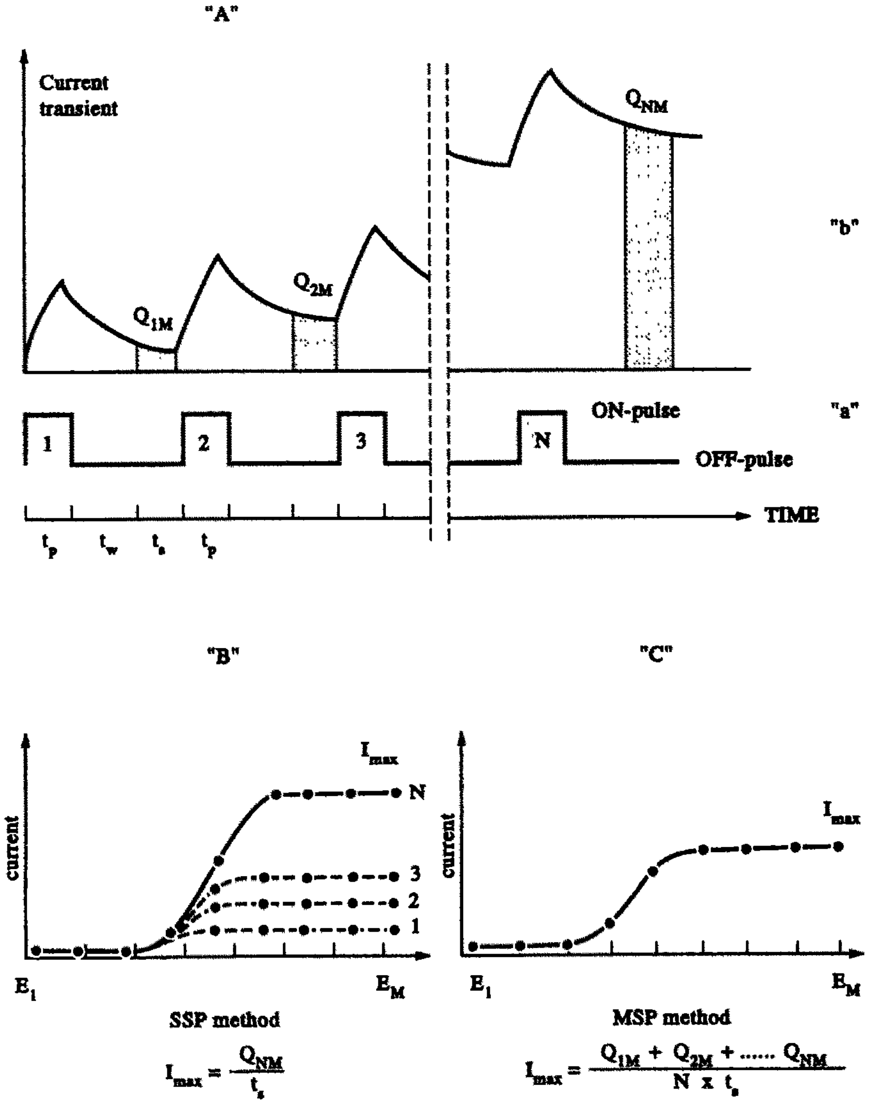

Fig. 4. Schematic procedure for recording the multiple sampling polarogram (MSP) using CGMDE electrode in the Computer Aided Experiment (CAE) and for the staircase technique. "A"—pulse sequence generating the Hg drop in a step-by-step mode ("a") and the resulting current transient profile ("b"). The measured charge samples "Q" at potential E_M are shown. The waiting time t_w, sampling time t_s, pulse time t_p and the number of pulses N are programmed in advance. The "N" determines the number of current samples to be summed up in the MSP method. "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). (For a more detailed explanation see text.)

The experiments have shown that the values of the signal to noise ratio are similar for both modes of "multisampling" measurement. The second mode was easier to realize using our instrument.

"Multisampling variant" has been named by us a "Multiple Sampling Polarography" and denoted by the symbol MSP. The principle of this method is illustrated in Fig. 4. 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} indicates the number of pulses required to generate a gravity controlled Hg drop and it is determined during electrode calibration. It can be seen from Fig. 4(b) and 4(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:

$$I_{\max} = \frac{Q_{1M} + Q_{2M} + \dots Q_{NM}}{N \times t}$$

whereas for the single sampling registration we get:

$$I_{\max} = \frac{Q_{NM}}{t}$$

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 on the example of selected polarographic techniques (staircase and differential pulse 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 5 presents the voltammogram and polarograms registered for 2 μM 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, accordingly, in the course of each Hg drop generation 10 charge samples were measured and summed up.

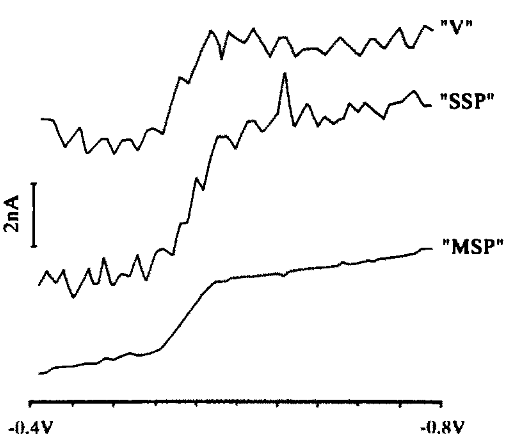

Fig. 5. Comparison of the "noise level"; voltamperogram (V), Single Sampling Polarogram (SSP), and Multiple Sampling Polarogram (MSP). The Hg drops were of the same size, generated by N corresponding to 10 pulses, with ON-pulse time 5 mesc N_{max} corresponds to 33 for a gravity-controlled Hg drop. Staircase technique, solution 2 μM Cd(II) in 0.1N KNO$_3$.

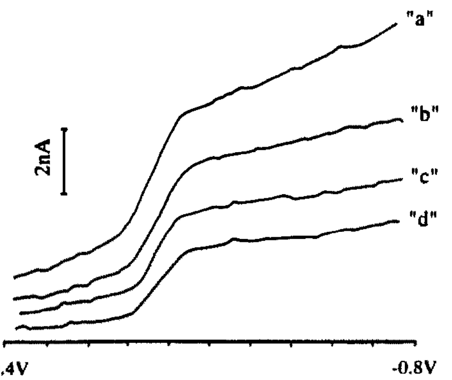

Fig. 6. Multiple Sampling Polarogram (MSP) for different waiting times; (a) 60 msec, (b) 100 msec, (c) 180 msec, (d) 260 msec. Staircase technique, solution and parameters of Hg drop generation as for Fig. 5.

A comparison of the staircase profiles from Fig. 5 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 voltammogram "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).

The successive measurements were intended to demonstrate how much the waiting time can be shortened in the "MSP" version. The Hg drops were generated as in the last experiment. The waiting time was shortened from 260 msec to 60 msec, which is illustrated by the MSP polarograms shown in Fig. 6. No increase in the perturbations level was observed even for the shortest waiting time. A successive study of the "MSP" method was intended to reveal the optimal number of charge samples to be summed up in order to significantly improve the S/N ratio. The Hg drops were generated by sequences of 5, 10, 15, 20 or 30 pulses. The "MSP" polarograms were recorded using staircase technique. A slight increase of perturbations was observed only for a polarogram recorded with summing up of five current samples, what can be seen from Fig. 7.

The measurements in the "MSP" method can be realized employing any of the measurement techniques, for instance DPP. Figure 8 shows profiles of DPP polarograms, registered by the SSP and MSP methods for 0.2 μM Cd(II) solution (cadmium ion concentration was chosen close to the detection limit for DPP technique). In both cases (SSP and MSP) the Hg drops were generated in the CGMDE variant by a sequence of 20 pulses. A distinct difference in the noise level can be seen, too.

The experiments described above have shown that the "noise level" is significantly reduced, if the CGMDE variant of Hg drop generation and the multiple sampling polarography method are used. This is evidenced by the profiles shown in Figs 5 and 8. The effect of the "noise level" decreasing was observed already after summing up of 10 charge samples, measured already after 60 msec of the waiting time.

CONCLUSION

The method of Hg drop generation in the step-by-step mode reduces significantly the undesirable convective perturbations of the diffusion layer accompanying the growing drop (such perturbations occur in excess when the Hg drop is generated in one step).

Owing to this advantage a few measurement variants can be performed.

(i) During the growth process the current can be sampled between each step or almost immediately (20 msec) after completion of the Hg drop which implies greater precision.

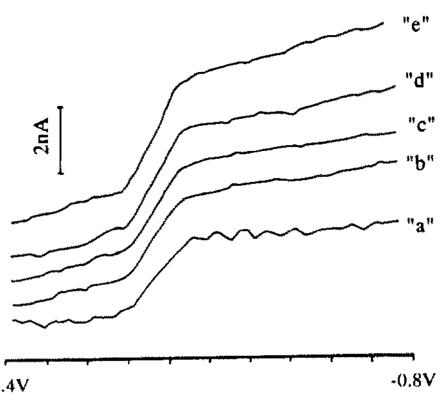

Fig. 7. Multiple Sampling Polarogram (MSP) for different numbers of current samples (N) to be summed up; (a) 5, (b) 10, (c) 15, (d) 20, (3) 30. Staircase technique, solution 2 μM Cd(II) in 0.1N KNO$_3$.

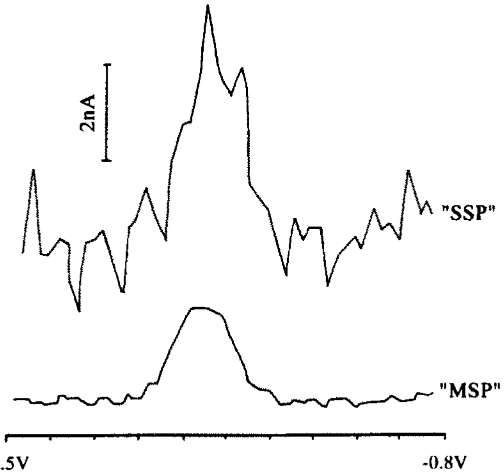

Fig. 8. Comparison of the "noise level" on recorded DPP profiles; "Single Sampling Polarogram" (SSP), and "Multiple Sampling Polarogram" (MSP). The Hg drops were of the same size and were generated by N corresponding to 20 pulses with ON-pulse time 50 msec. N_{max} corresponds to 90 for a gravity-controlled Hg drop. DPP technique with dE -20 mV, solution 0.2 μM Cd(II) in 0.1N KCl.

(ii) The current samples can be used for recording the current–time profiles or for amperometric study.

(iii) The current samples after their summing up can be considered as a signal of increased size, as the observed noise level caused by averaging the perturbation effects is significantly low.

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