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Determination of Cadmium in the Presence of Surfactants with the Controlled Growth Mercury Electrode

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An electroanalytical procedure for the solutions contaminated with surface-active substances (SAS) is presented. The procedure is based on current-time curves (recorded within a step-like growing period of the Hg-drop) which enable the minimization or even elimination of systematic errors resulting from an accidental contamination with SAS. A practical application is demonstrated with 0.1mmol l^{-1} Cd(II) solution contaminated with Triton X–114 or 3,4-dichlorobenzyltriphenylphosphonium chloride (Eulan) as the selected surface-active substances.

Zaprezentowano procedurę elektrochemicznej analizy roztworów zanieczyszczonych związkami powierzchniowo aktywnymi. Procedura ta, wykorzystująca krzywe prąd–czas (rejestrowane w czasie skokowego narastania powierzchni kropli Hg) pozwala zminimalizować lub nawet wyeliminować błędy systematyczne, będące wynikiem przypadkowego zanieczyszczenia roztworu związkami powierzchniowo aktywnymi. Praktyczne zastosowanie pokazano na przykładzie 0.1 mmol l^{-1} roztworu Cd(II) zawierającego różne ilości Tritonu X–114 lub Eulanu.

Key words: current-time curve, controlled growth mercury electrode, surfactants, electroanalysis, determination of Cd(II)

Contamination of the solution with natural or synthetic surface-active substances (SAS) involves a dumping effect of the faradic current in polarography and voltammetry, which causes a serious analytical error. Such undesired effects can be detected by shape analysis of the current-time curves [1–4]. Investigation of the current-time curves (*i–t* curves) recorded within the growing period of the single Hg-drop of the dropping mercury electrode (DME) was a subject of interest of many electrochemists at the end of the 1950s [1]. The shape of such curves (*i.e.* the shape of current *vs* time dependence) is influenced by the geometry of the growing Hg-drop and electrode process features. The results obtained were promising – the shape or changes in the shape of the current-time curve can be used to distinguish between diffusion-controlled electrode processes, kinetic processes or catalytic processes. Additionally, the effects of adsorption of the surface-active substances upon the electrochemical process was easy to detect.

For comparison of the results, the shape of the current-time profiles were described mathematically, usually by specifying the b exponent value for the equation:

$$i_t = at^b,$$

where t is the growth time counted from the beginning of the single drop, i_t is the adequate instantaneous current value and a is a proportionality coefficient.

In the case of diffusion-controlled processes (assuming an absence of charging current and disturbances caused by SAS) the exponent value should be equal to 1/6, as predicted by Ilkovic's equation. Such a value of the exponent is, among other things, the result of the Hg-drop area growth (which causes a current increase proportional to $t^{2/3}$) and a depletion of the electroactive species around the electrode, due to electrolysis (which should cause the current to drop proportional to $t^{-1/2}$). As the last process within the time of the Hg-drop growth undergoes different disturbances, the expected exponent value was not constant, and it changes within some range depending on the experimental conditions. In practice, the exponent values of the *i–t* curves recorded within the growing period of the Hg-drop of the DME varied from about 1 at the initial stage of the Hg-drop life (the smallest faradic to charging current ratio) up to 1/5 at the end of the drop life. Additionally, there was a wide discrepancy in the results reported from different laboratories. For these reasons no practical application could be found for the current-time curves and their investigation was given up. New possibilities of such research have opened the Controlled Growth Mercury Electrode CGME [4–7]. In this electrode the mercury outflow is controlled by a fast response valve, actuated by a single pulse or pulse sequence with on-pulse time as short as 1 msec. The sequence of short pulses that actuate the valve involve a step-by-step Hg-drop increase. In practice, such a step-like Hg-drop increase can be realized by several hundreds of a small Hg-drop size increments (from the beginning of the Hg-drop generation up to its gravity-controlled maximal size). The current response during Hg-drop generation using the step-by-step mode may be recorded as a sequence of current samples corresponding to successive stages of the Hg-drop area development. Such a relation is similar to the *i–t* curve recorded in the past within the growing period of the Hg-drop of the DME [4,7]. In difference, such a method of Hg-drop generation enables the synchronization of the polarizing voltage programme and current sampling procedure with Hg-drop growth.

A few advantages should be expected if the *i–t* curves are recorded on the step-by-step increasing Hg-drop of CGMDE:

– current-time curves may be recorded even for very low depolarizer concentrations because the current samples can be measured during off-pulse time, when the

Hg-drop area is constant and the charging current is very low;

– Hg-drop growth time may be programmed in advance and changed within the range of a few tens of milliseconds up to few hours;

– the diffusion layer depletion around the Hg-drop is under experimental control, now – "the first drop conditions" recommended in the past can be obtained at any desired time.

The presented work shows, on the basis of the selected examples, how the undesirable influence of SAS adsorption on analytical results can be eliminated. Since the measurements were performed for solutions contaminated with a rather large amount of SAS, the fast Hg-drop growth rate was programmed [7].

EXPERIMENTAL

Instrumentation

A multipurpose electrochemical analyzer, model EA–9 (MTM Poland), coupled with a personal computer *via* a specialized, bi-directional interface was used in all experiments. A CGME electrode equipped with a 150 μm I.D. bevelled capillary (manufactured by Bioanalytical Systems Inc., USA) was used for the current-time curve registrations.

The MTM–Poland EAGRAPH software (for MS WINDOWS) provided the electrochemical measurements, data acquisition and advanced results processing.

The EAGRAPH measuring the program inputs initial parameters, checks their validity, performs measurements according to initial data and displays the results on the monitor. If necessary, the displayed plot is rescaled during the measurements so that the whole curve is visible all the time.

All potential values can be programmed with 1mV resolution and all times with 1msec. resolution.

For CGME the programme includes:

– procedures for Hg-drop generation, procedures for Hg-drop calibration and recalibration [4],

– different variants of measurements with CGME as the working electrode. One of them allows the *i–t* curve registration.

The EAGRAPH software provides advanced interpretation of the recorded current-time relations. For example, the k and b coefficients of equation $i_n = kn^b$ can be determined (i_n is the current value measured after the valve was opened n-times, n is the number of actuating pulses counted since the moment the Hg-drop generation began, k is a proportionality coefficient and b is the shape parameter).

Current samples taken after successive drop increments and with a delay adequate for charging current decay were displayed in the form of current samples *vs* number of increments, which represents the current-time relation known from earlier studies [1].

The shape parameters of the particular fragments of the *i–t* curve were determined and listed in the tables. The chosen fragment was symbolized by the number of pulses, for example 1–3, 3–5, 5–7,...

Procedure

Prior to the *i–t* curve registrations a series of gravity-controlled mercury drops were dispensed by a sequence of pulses of adequate duration. The number of pulses was counted and stored for further Hg-drop size recalibration procedure [4]. To ensure the spherical shape, the Hg-drop did not exceed 35% of the gravity-controlled maximal drop.

Cell and electrodes

An one-compartment three-electrode cell with a CGME working electrode, an Ag/AgCl/3 mol l^{-1} KCl reference electrode and platinum wire with area of about 0.5 cm^2 as anauxiliary electrode were used. All solutions were deaerated and blanketed with argon gas before use. The room temperature was 20 +/– 1°C.

Reagents

All reagents used in the experiments were of analytical grade. The solutions were prepared using four times distilled water (the last two steps from quartz). Triton X–114 (Aldrich Chemie) and 3,4-dichlorobenzyl triphenylphosphonium chloride (Eulan) was used as received.

RESULTS AND DISCUSSION

The principle of the procedure for the current-time curve registration (under large amplitude pulse excitation voltage) is shown in Figure 1. The procedure followed has been previously described in details [7].

As can be seen, the Hg-drop is generated in the step-by-step mode by a programmed sequence of n actuating pulses each of t_p duration. The time intervals between subsequent pulses are equal to $t_1 + t_2 + t_3$. The reduction of the depolarizer to be determined took place after a polarizing pulse with amplitude E_S and duration $t_2 + t_3$ was applied. Within the duration of each polarizing pulse the charging current decayed to a very low value during the t_2 time interval. The current sample free from a capacity component was then taken during the t_3 period. Next, within the $t_p + t_1$ period the previously reduced depolarizer was oxidized under E_B potential.

The current samples i_F, measured after each subsequent Hg-drop size increment were displayed in the form of current-time or current-number of pulses' dependence.

As can be seen from Figure 1, anodic oxidation of the previously reduced depolarizer allowed for regained it, and as a result, the concentration gradient around the Hg-drop was cancelled before the next current sampling procedure had been performed. In this case the sampled current should reflect the changes of the Hg-drop area only, because $c_{\mathrm{surface}} = c_{\mathrm{bulk}} = \mathrm{const}$, t_2 and t_3 were the same each time and the capacity current disturbances were very small. This means that the value of the shape parameter b for such current-time relations, recorded for ultrapure, free from surface-active substances solutions, should be close or equal to 2/3 and independent of depolarizer concentration.

The shape of such i–t curves reflect the Hg-drop area increase and the current samples are not disturbed by charging component what was proved by registration of the i–t curves for ultrapure Cd(II) solutions with different concentration, ranging from 2.5 μmol l^{-1} up to 0.5 mmol l^{-1}. The extensive range of the cadmium concentration did not have any essential effect on the values of the shape parameters. For example, Figure 2 shows the i–t curves recorded for the solutions with Cd(II) concentration equal to 0.036 mmol l^{-1}, 0.066 mmol l^{-1}, 0.099 mmol l^{-1}, 0.196 mmol l^{-1} and 0.476 mmol l^{-1}, and Table1 shows the shape parameter values for these i–t curves.

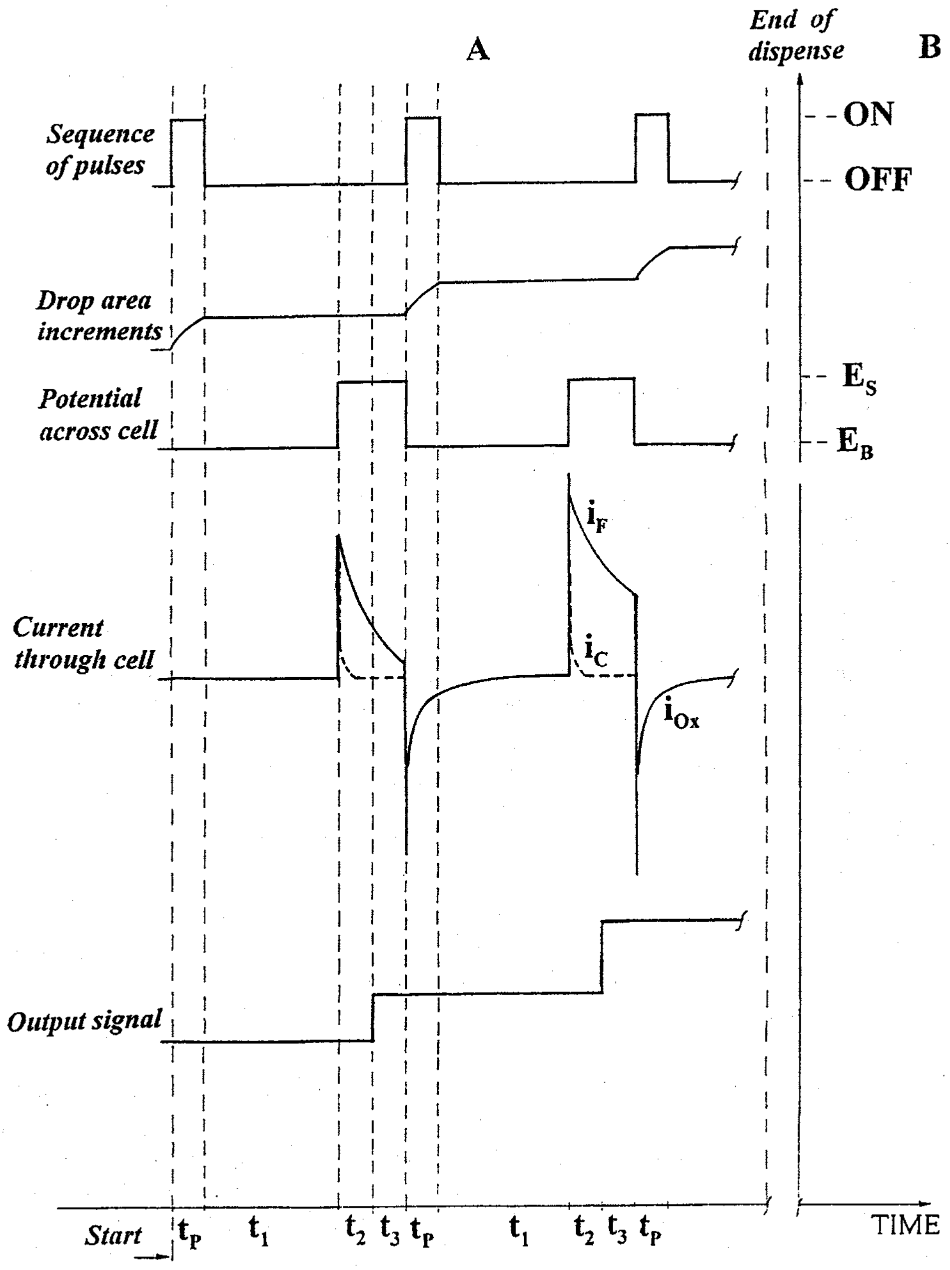

Figure 1. The *i–t* curve registration diagram – timing sequence during Hg-drop generation and current measurement: E_S – step potential; E_B – base potential; t_P – on-pulse time; t_1 – quiet and amalgam oxidation time; t_2 – waiting time, the charging current decays to low value; t_3 – sampling time; i_F – faradic current profile (diffusion limited); i_C – charging current profile; i_{Ox} – amalgam oxidation current profile

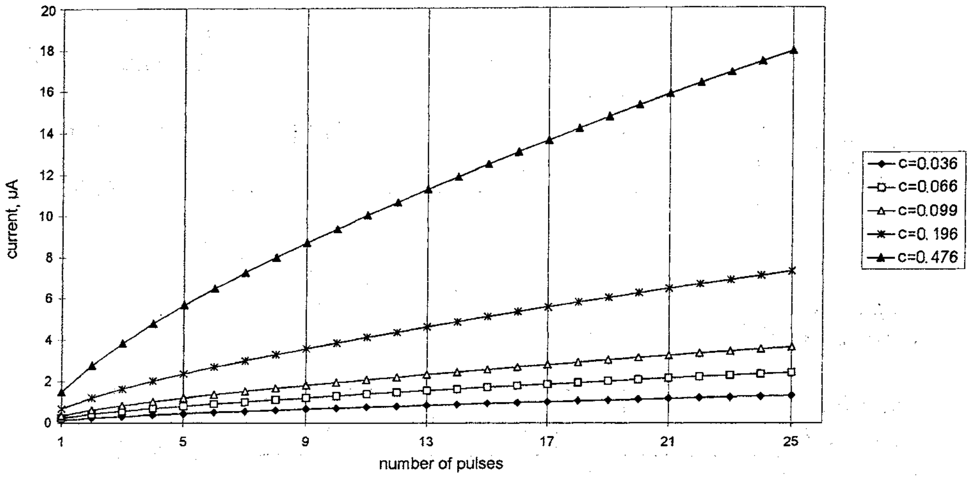

Figure 2. The set of *i–t* curves recorded for Cd(II), 0.1 mol l^{-1} KNO_3 solutions with different Cd(II) concentration *c* (indicated above in mmol l^{-1}). Each Hg-drop of the CGME was generated by a 25-pulse sequence within a 3.75 s time interval and under 200 mm Hg column pressure; t_1 = 100 ms, $t_2 = t_3$ = 20 ms, t_P = 10 ms

Table 1. Shape parameters of the *i–t* curves recorded for ultrapure Cd(II), 0.1 mol l^{-1} KNO_3 solutions with different Cd(II) concentration. Each Hg drop of the CGME was generated by 25 pulses within 3.75 s time interval

Cd(II) concentration mmol l^{-1}	Calculated shape parameters for individual subranges of the *i–t* curves					
	0–4	4–8	8–12	12–16	16–20	20–24
0.036	0.724	0.691	0.678	0.693	0.677	0.688
0.066	0.716	0.688	0.681	0.688	0.695	0.686
0.099	0.715	0.698	0.688	0.696	0.698	0.689
0.196	0.714	0.703	0.697	0.699	0.699	0.691
0.476	0.717	0.709	0.711	0.708	0.707	0.704

E_S = –0.75 V, E_B = –0.4 V, t_1 = 100 ms, $t_2 = t_3$ = 20 ms, t_P = 10 ms.

As can be seen, each of them is close to 2/3. Some excessive values of shape parameters for the initial fragments of the current-time curve are thought to be the results of the low pressure mercury column (200 mm). Back pressure, caused by surface tension of the growing drop, decreases the rate of the mercury flow through the capillary. This effect is most significant when the radius of the drop is very small (since the "back pressure" is proportional to 2δ/r – where δ is the interfacial tension and *r* is the radius of the drop), *i.e.* at the early stage of the current-time curve registration. As was expected, after increasing the mercury head pressure up to 600 mmHg, the recorded *i–t* curves had a shape parameters value close to 2/3, practically within the whole range of the curve. Since all the results obtained under low and high-mercury pressure are very reproducible, both low and high-mercury head pressure were used in this work.

An effect of rather high Triton X–114 concentration on the shape of the *i–t* curves is shown on Figure 3 The *i–t* curves presented here were recorded for a solution with constant Cd(II) concentration, equal to 0.099 mmol l^{-1}, but contaminated with a different amount of Triton X–114. The measuring conditions were the same as for Figure 2. One can see here the dumping effect on faradic current, caused by Triton X–114 adsorption. It should be noticed that initial fragments of the *i–t* curves are not disturbed even in the presence of a large amount of Triton X–114 and the shape parameters for them are close to 2/3. The shape parameter of these curves, presented in Table 2 proves this observation.

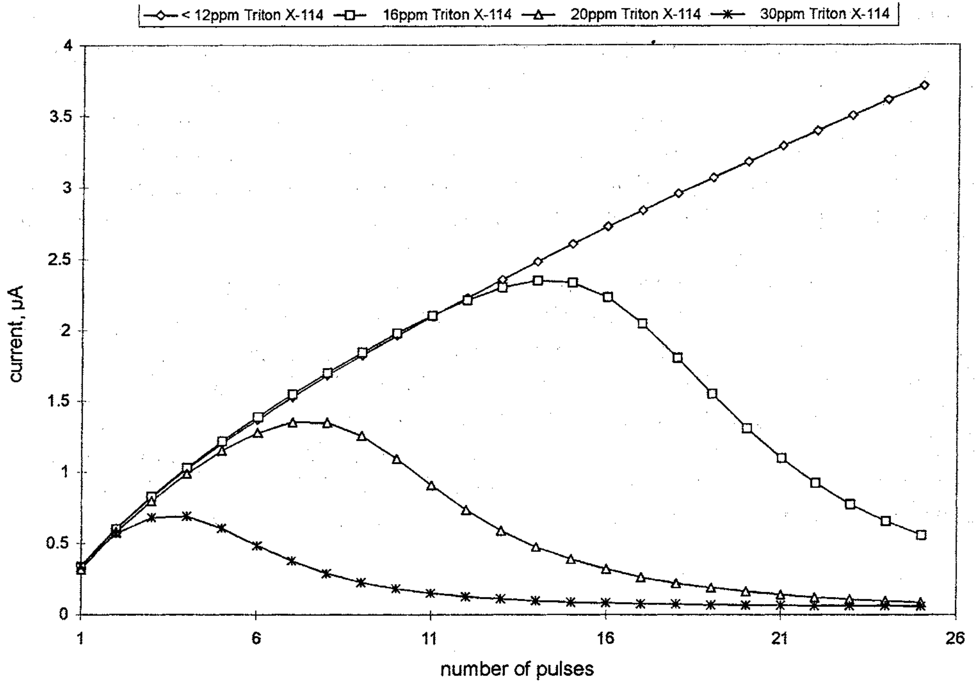

Figure 3. The *i–t* curves recorded for 0.099 mmol l^{-1} Cd(II), 0.1 mol l^{-1} KNO_3 solution contaminated with different amounts of Triton X–114 (indicated above). Each Hg-drop of the CGME was generated by a 25-pulse sequence within a 3.75 sec time interval and under 200 mm Hg column pressure: $t_1 = 100$ ms, $t_2 = t_3 = 20$ ms, $t_P = 10$ ms

Table 2. Effect of additive Triton X–114 on the shape parameters of the *i–t* curves recorded for the solution 0.099 mmol l^{-1} Cd(II), 0.1 mol l^{-1} KNO_3. Each Hg drop of the CGME was generated by 25 pulses within 3.75 sec time interval

Triton X–114 ppm	Calculated shape parameters for individual subranges of the *i–t* curves					
	0–4	4–8	8–12	12–16	16–20	20–24
0	0.716	0.706	0.701	0.699	0.698	0.696
12	0.725	0.714	0.707	0.701	0.703	0.699
16	0.711	0.707	0.606	–0.411	–2.961	–3.868
20	0.701	0.177	–2.067	–3.014	–2.922	–2.644
30	0.288	–1.694	–1.949	–1.282	–0.766	–0.401

$E_S = -0.75$ V, $E_B = -0.4$ V, $t_1 = 100$ ms, $t_2 = t_3 = 20$ ms, $t_P = 10$ ms.

On the basis of such an observation the electroanalytical procedure for the solutions contaminated with surface-active substances has been proposed.

Essence of the proposed electroanalytical procedure is following:

An *i–t* curve recorded within the period of the step-by-step generation of the Hg-drop represents a set of *n* current values for *n* subsequent Hg-drop area increments. A set of such *i–t* curves, recorded for ultrapure solutions with different and known depolarizer concentrations, enables establishing *n* calibration curves for *n* different Hg-drop areas. As example, Figure 4 shows such calibration curves, derived on the basis of *i–t* curves from Figure 2, for selected areas of the Hg drop (indicated on Fig. 2 by the vertical line).

An *i–t* curve recorded under the same conditions for a solution contaminated with surface-active agents may be partially (or totally) disturbed. Determination of the depolarizer concentration should be preceded here by an *i–t* curve registration and the determination of its shape parameters. On this basis, a maximal undisturbed current value should be found and the appropriate calibration curve (recorded for the same Hg-drop area depletion) should be chosen to determine an unknown concentration.

Figure 5 shows a procedure algorithm. First of all the set of *i–t* curves for ultrapure standard solutions with different and known depolarizer concentrations should be recorded and stored (calibration step). After that, the procedure checks if the shape parameter values of such curves are close to 2/3. If so, the next stage is to ascribe to each *i–t* curve, the proper depolarizer concentration. On this basis, a set of calibration curves is generated and stored. The number of calibration curves is proportional to the number of energizing pulses used for a particular Hg-drop generation. At this moment, the procedure is ready for a measurement.

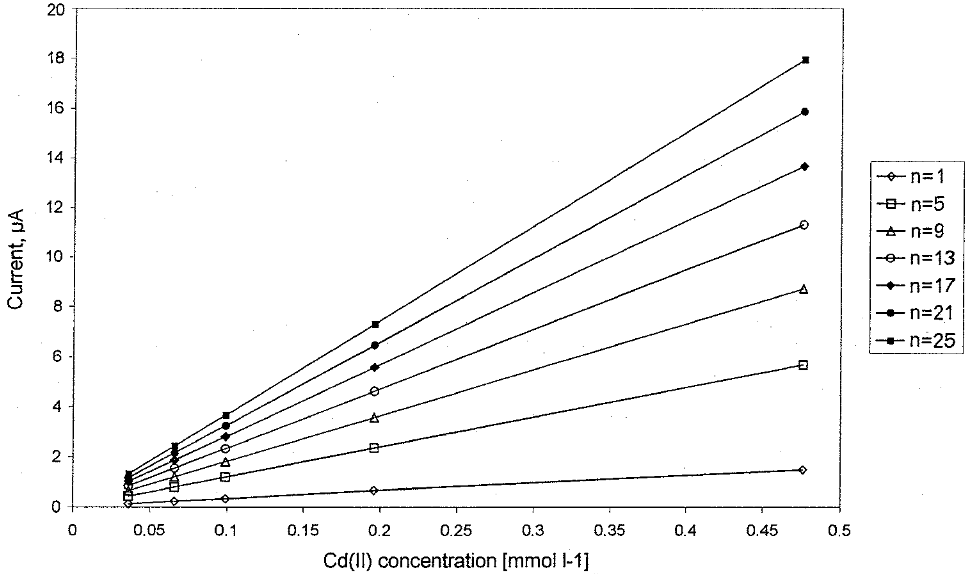

Figure 4. The set of calibration curves for selected areas of the Hg drop derived on the basis of *i–t* curves from Figure 2. The chosen drop areas are described by number of energizing pulses *n* and additionally indicated on Figure 2 by vertical line

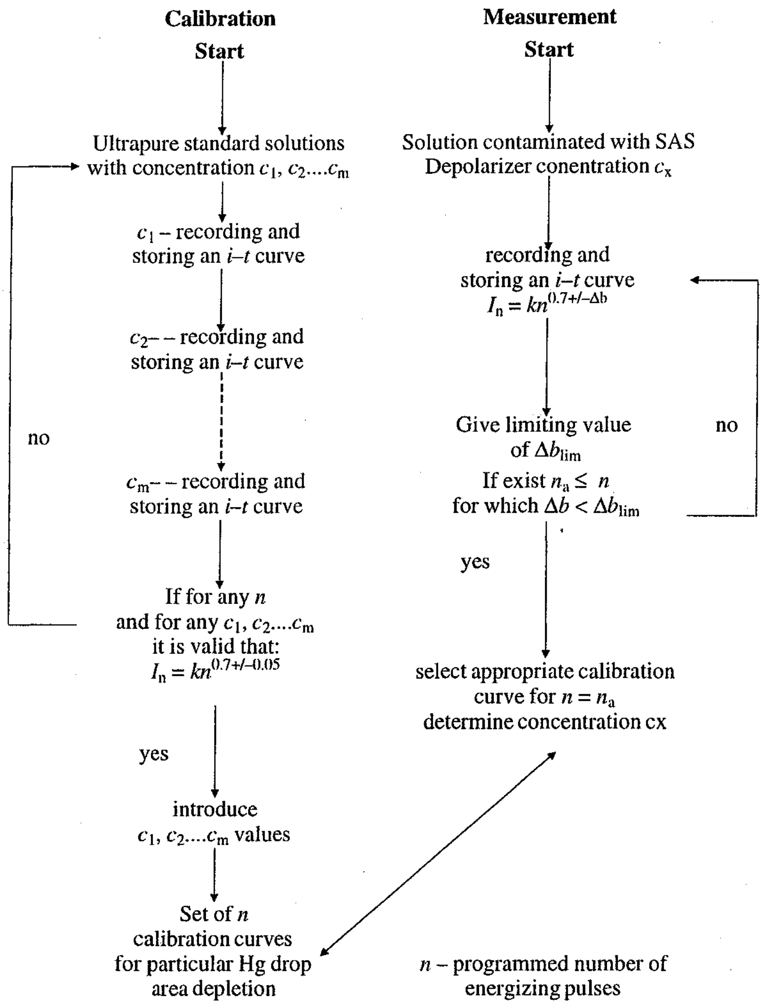

Figure 5. Algorithm of the electroanalytical procedure for the solutions contaminated with surface-active substances

The measurement begins also from the *i–t* curve registration. The users have to introduce an acceptable limiting value of the shape parameter, *e.g.* 0.65 (*i.e.* $\Delta b_{\lim} \leq 0.05$, see Fig. 4). After the *i–t* curve has been recorded for the investigated solution, the procedure checks whether such values of the shape parameter exist and up to which stage of the Hg-drop area depletion these come true. If, for example, the shape parameter value was higher than 0.65 up to the Hg-drop area depletion caused by 19 pulses, the procedures choose the calibration curve for the same Hg-drop area depletion and on this basis the depolarizer concentration is determined.

The practical application of this procedure was checked using 0.099 mmol l^{-1} Cd(II), 0.1 mol l^{-1} KNO_3 solution contaminated with different amounts of the selected surface-active agents, such as Triton X–114 and Eulan. As an example, Figure 6 shows the *i–t* curves recorded in the presence of different and rather large amounts of Eulan. Tables 3 and 4 illustrate an example of the use of this procedure for determining the depolarizer concentration in a solution contaminated with surface-active agents. The presented data illustrates how long the shape parameter values of such curves were larger than the chosen limiting value (here $b > 0.65$). The Cd(II) concentrations calculated on the basis of the selected calibration curve are also shown. The calculated Cd(II) concentrations were close to the true value (0.099 mmol l^{-1}), even in the case of the highest concentration of SAS.

Table 3. Example of practical application of the described procedure for the determination of Cd(II) concentration. Solutions contaminated with different amount of Triton X–114. Real Cd(II) concentration – 0.099 mmol l^{-1}, 0.1 mol l^{-1} KNO_3. Each Hg drop of the CGME was generated by 25 pulses within 3.75 s time interval

Triton X–114 ppm	Shape parameter value > 0.65 up to *n*	Determined Cd(II) concentration mmol l^{-1}
0	25	0.100
8	25	0.098
12	25	0.099
16	14	0.095
20	6	0.093
30TT	2	0.092

$E_S = -0.75$ V, $E_B = -0.4$ V, $t_1 = 100$ msec, $t_2 = t_3 = 20$ msec, $t_P = 10$ msec.

Table 4. Example of practical application of the described procedure for the determination of Cd(II) concentration. Solutions contaminated with different amount of Eulan. Real Cd(II) concentration – 0.099 mmol l^{-1}, 0.1 mol l^{-1} KNO_3. Each Hg drop of the CGME was generated by 25 pulses within 2.55 s time interval

Eulan ppm	Shape parameter value > 0.65 up to *n*	Determined Cd(II) concentration mmol l^{-1}
< 6.5	25	0.098
26	8	0.099
39	5	0.096
52	3	0.092
65	2	0.084
100	–	–

$E_S = -0.75$ V, $E_B = -0.4$ V, $t_1 = 60$ ms, $t_2 = t_3 = 20$ ms, $t_P = 2$ ms.

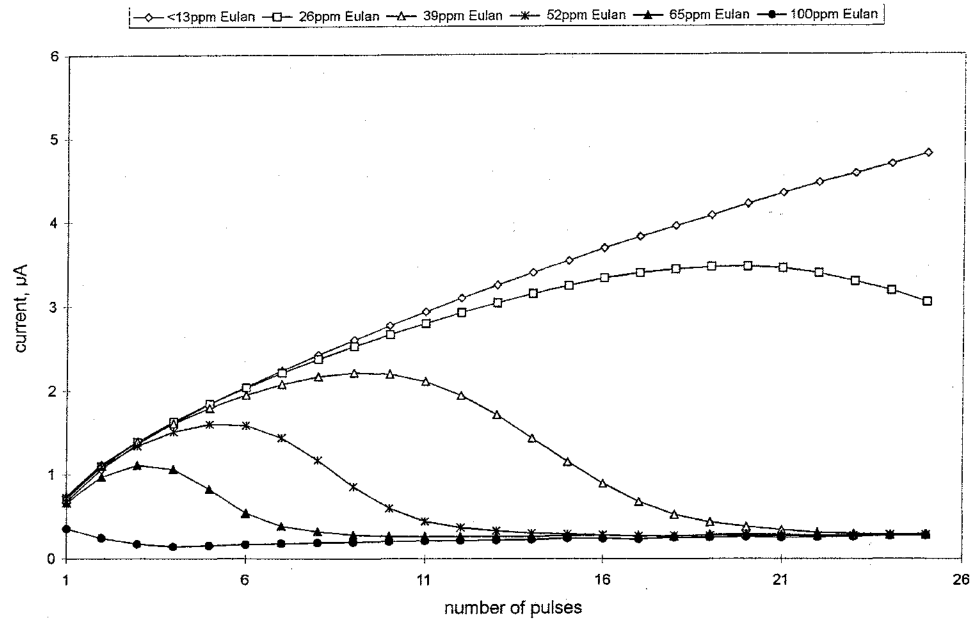

Figure 6. The *i–t* curves recorded for 0.099 mmol l^{-1} Cd(II), 0.1 mol l^{-1} KNO_3 solutions contaminated with different amounts of Eulan (indicated above). For the highest Eulan addition (100 ppm), determination of cadmium concentration was impossible. Each Hg-drop of the CGME was generated by a 25-pulse sequence within a 2.55 sec time interval and under 600 mm Hg column pressure: $t_1 = 60$ ms, $t_2 = t_3 = 20$ ms, $t_P = 2$ ms

CONCLUSIONS

The proposed procedure enables the minimization or even elimination of the systematic errors caused by current dumping, resulted from an accidental contamination of the solution by large amounts of SAS. Calibration as well as measurements are preceded by *i–t* curve registration and determination of its shape parameters. On this basis, measurement parameters can be selected for which any measurable effects of the current dumping are not observed and, at the same time, the measured current is as high as possible.

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