

New mathematical method for detection of the metal-catalyzer traces on the modified electrodes surface

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Abstract

New mathematical approach for characterization of the measured voltammograms (VAGs) obtained for electrodes with catalytic response and modified by nanoparticles of gold (Au) and palladium (Pd) was applied. The cases with tracing concentrations of the electrodeposited catalyzer were considered, when the corresponding VAGs for the solutes containing catalyzer and background coincide practically with each other. Using the catalyzer electrode response of dopamine (DA) and new mathematical approach for description of the remnant current fluctuations, it was shown that becomes possible to extract a useful information from the measured VAGs because of increasing the limits of the signal/noise ratio. The fluctuations of the remnant currents are transformed into a specific “confidence tube” that is used for detection of the VAGs perturbations evoked by the presence of the analyte traces. Using the proposed mathematical method, it becomes possible to achieve the low boundary of the DA detection up to 10⁻⁸ M.

Keywords: Mathematical Method; Confidence tubes; Chemically Modified Electrode; Electro-Catalytic Oxidation; Dopamine

The list of the basic acronyms

CME – chemically modified electrode

CT(s) – confidence tube(s)

DA – dopamine

GCE – glassy carbon electrode

POLS – procedure of the optimal linear smoothing

SRA – sequence of the ranged amplitudes

TF – trendless fluctuations

VAG(s) – voltammogram(s)

Introduction

It is known that chemical modification of the electrodes surface for voltamperometry, including sensors with amperometric response, allows enhancing the sensitivity for analyte detection and increase its dynamic concentration range [1-3]. In the last time, there is an interest to the chemically modified electrodes (CME) with immobilized micro/nano-catalyzers having metallic origin for organic synthesis [3]. Their application leads to increasing of the registered current and in the same time to decreasing of the overstrain oxidation of organic compounds.

In spite of variety materials used for creation of the CME the gold and metals belonging to the platinum group are remained as the most used metals for their creation [4]. There are two factors that determine their wide usage: (a) high catalyst activity and (b) available technology for their proper modification. Experimental

research made in this direction shows that for achieving the maximal catalyst effect it is necessary to find the proper working conditions for their modification. These working conditions are related to the content of the electrolyte background, concentration of the used metal, the technology of the catalyst layer creation (electrolytic time) and other factors [3]. One can say that in the general case the catalyst current is determined presumably by the particle sizes involved in the catalyst process and their concentration on the electrode surface [5]. However, these factors depend on the time that is needed for their formation on the electrode surface. In research of this phenomenon the undoubted interest associated with evaluation of the catalysts “remnant traces”, which can “work” and give a small amperometric response on the given substrate. It is necessary to note that in spite of sufficient number of publications [2, 3, 6-8] associated with the analysis of the properties of the CMEs, the papers related to the evaluation of the catalyst effect in the limits of possible background current fluctuations (the so-called electrochemical “noise”) are practically absent.

In this paper, we propose a new statistical method for detection of the catalyst amount on its tracer-detectable level. The presence of the detectable catalyst is not fixed on the recorded VAGs because the registered curves coincide practically with the background VAGs. The basic attention was paid to electrochemical deposition of the gold (Au) and palladium (Pd) particles as potential catalysts on the surface of the glassy carbon electrode (GCE) and description of new

mathematical method allowing to evaluate a set of small factors that determine the useful/registered signal. Based on the results obtained in this paper, one supposes the high-sensitive sensor on DA detection, which serves as a biomarker of the following central nerve system diseases as the Alzheimer's sclerosis, Parkinson's disease, depression, schizophrenia etc.

Experimental section

Reagents

Electrodeposition of metals on an electrodes surface was realized from the solutes containing palladium chloride PdCl_2 (Aldrich company) and chloroauric acid HAuCl_4 (Aldrich company) on the background of $0.01 \text{ M H}_2\text{SO}_4$.

Initial water solutes of PdCl_2 , HAuCl_4 and DA are prepared of dilution of their accurate sampling. As the background electrolyte we used 0.1 M solute of H_2SO_4 and background phosphate buffer (pH 6.86).

Equipment

The registration of the cyclic VAGs was realized with the help of three-electrode scheme with the usage of potentiostat/galvanostat CHI600E (USA). As the working electrode we used GCE and CMEs with electrically deposited palladium (Pd-GCE) and gold (Au-GCE) particles. The platinum wire and silver-chloride electrode (Ag/AgCl (3.0 M NaCl)) were used as auxiliary and comparison electrodes, accordingly.

The electrode modification by metal particles

The deposition of metal particles on the CGE surface was realized by the potentiostatic electrolyze method at the applied potential -0.4 V for palladium and -0.3 V for gold. Before modification procedure, we realized the preliminary preparation of the GCE surface: the given electrode was grinded with the help of abrasive materials, filter paper and tracing papers, accordingly. Then after that, the bidistilled water washed the used GCE away.

Experimental methodology

Each experiment includes 100 successive measurements of the cyclic VAGs in the continuous conditions. The mechanical regeneration of the working electrode surface was absent. The registration of the cyclic VAGs was realized in the applied potential range $[0, 1.3] \text{ V}$, the potential scanning rate was equaled to 50 mV/s . All cycles were performed at room temperature. Initially, 100 VAGs were registered in the background electrolyte with the usage of non-modified GCE. Then, not taking out the registered three-electrode system from the solute, the certain DA volume was imbedded and 100 cyclic VAGs were registered again.

Similar experiment was performed on the electrodes modified by metal particles (Pd-GCE, Au-GCE), preliminary precipitating the modifier on the electrode surface electrochemically.

Results and discussion

Electrochemical behavior of electrodeposited palladium and gold nanoparticles

On an anode branch of the cyclic VAG obtained on the electrode with electrodeposited particles of Au and Pd in the "oxygen" potentials region the anode-cathode maximal current values are registered. They are related to absorption/desorption of hydroxides-ions and with oxidation of metals up to the corresponding oxides

and hydroxides.

The electrochemical properties of metals deposited on GCE depend on the pH medium. With increasing of the pH value one can observe the essential decreasing of the peaks heights and displacement of the potentials in the anode region. Earlier [9], the working conditions of the VAGs registration with the usage of GCE modified by Pd particles in the presence of $0.1 \text{ M H}_2\text{SO}_4$ was established. The GCE modified by Au particles one can apply in acid, neutral and alkaline electrolyte solutes. The most stable response is observed in a neutral solute.

In papers [9, 10] the working conditions were found for metal nanoparticles electrodeposition. It was shown that the decreasing of electrolysis time and metal salts concentration in a deposition solute leads to the size particles decreasing together with similar behavior of the registered oxidation modifier current value. As an example, we show in Figs.1 the dependencies of the limiting current at $E = 0.70 \text{ V}$ obtained on the Pd-CME vs. the Pd salt concentration (Fig.1, b) and electrolysis time (Fig.1, c).

It was established also that the decreasing of the metal salts concentration in the deposition solute for the concentration range $[5 \times 10^{-3}, 1 \times 10^{-4}] \text{ M}$ the current value decreases. In further decreasing of the metal salts concentration, the form of the VAG does not differ visually from a similar VAG obtained for the non-modified electrode (Fig.1, a).

For confirmation of the trace metal-catalyst presence on the electrode surface the new mathematical approach was used. It is useful for detection of small concentration of a some "mixture" (the presence of metal particles on the electrode surface in our case) on the stable buffer/background solute. We compared the parameters characterizing the VAG behavior of the GCE modified by nanoparticles of Au/Pd, correspondingly, at their small concentrations. In particular, we analyzed the VAG responses on the non-modified electrode (used as the background) and Au-GCE and Pd-GCE. Experiments were performed in the $0.1 \text{ M H}_2\text{SO}_4$ solute or phosphate buffer background at pH=6.86 and continuous data registration covering 100 successive cycles.

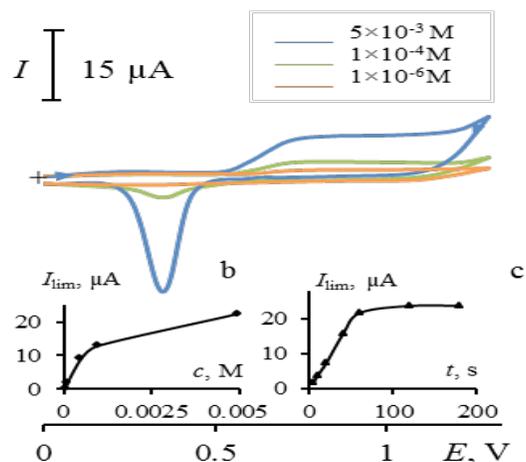


Figure 1: Cyclic voltammograms obtained at Pd-GCE during electrodeposition of palladium particles at $E_c = -0.40 \text{ V}$ (at $t_c = 5 \text{ s}$) from $5 \times 10^{-3} \text{ M}$, $1 \times 10^{-4} \text{ M}$ и $1 \times 10^{-6} \text{ M}$ PdCl_2 solution in the background

0.1 M H₂SO₄ (a); the dependence of the current maximum at E 0.70 V in the voltammogram on Pd-GCE on the concentration of PdCl₂ in the deposition solution (b) and the metal deposition time (c)

Mathematical part: Description of the new mathematical method

In this section, we want to propose new method for the traces detection based on the creation/calculation of the so-called confidence tubes CT(s). The idea of this method can be expressed with the help of the following steps. Let us suppose that we have some measured curve (in our case this curve coincides with the registered VAG).

S1. We apply the procedure of the optimal linear smoothing (POLLS) that helps to obtain the pseudo-fitting curve. The corresponding mathematical expressions helping to obtain the smoothed curves were given earlier and explained in papers [11-12]. These curves for a buffer solution are shown in Fig.2.

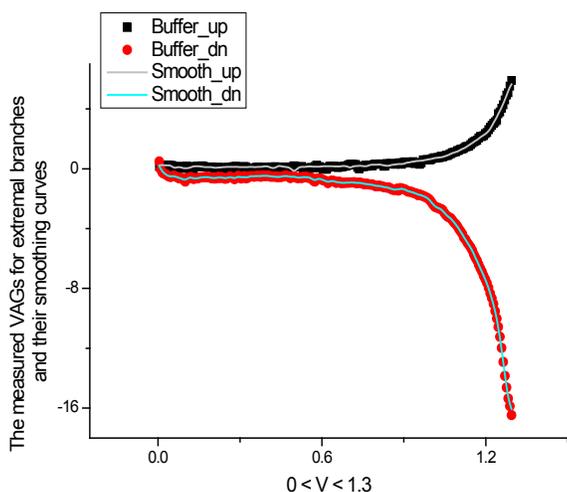


Figure 2: The branches corresponding to maximal and minimal curves for buffer solution. The smoothed curves are shown by bold lines

S2. After calculation of the smoothed curves that are very close to the measured ones, (the Pearson correlation factor equals 0.99 or even more) we subtract them from the measured curves and obtain the trendless fluctuations (TF) that serve as specific "detectors" for detection of possible traces. These TF oscillate relatively horizontal OX axis and has positive/negative amplitudes, respectively.

S3. We collect all possible amplitudes in the form of the sequence of the ranged amplitudes (SRA) when all positive amplitudes are located from the left-hand side to the right one in the descending order ($y_1 > y_2 > \dots, y_N$). The same procedure is realized for the negative amplitudes, however, the corresponding SRA ordered from the left to the right-hand side has negative sign and forms the sequence of the amplitudes taken in the ascending order ($-y_1 < -y_2 < \dots, -y_N$). Supposing that all fluctuations are located in the limits of the maximal range $Rg(+,-) = \max(y_+) - \min(y_-)$ and corresponding to the chosen sampling, (incorporating 100 VAGs) one can obtain the CT-1.

S4. Integration of each branch formed from the corresponding SRAs allows us to obtain the CT-2. The range $Jr(+,-) = \max(Jy_+) - \min(Jy_-)$ serves as the specific quantitative label of the second order for detection of possible substance trace.

Really, if the range values of the CT(s)-1,2 obtained from the VAGs correspond to the influence of "a trace" perturbation and are located inside the CT(s)-1,2 corresponding to the given background, then, in this case, any perturbation considered as an external factor is not detectable. In the opposite case, when the both ranges of the background are less than the ranges of the CT(s)-1,2 evoked by perturbation then it can be detectable. The first application of this methodology based on the analysis of the CT-1,2 was described in paper [13]. We want to notice that these traces detection method is rather "universal". It can be applied for a wide class of the measured spectral/response curves and takes into account the peculiarities of the measured equipment. This method is very simple and allows to compare the "pattern" equipment (or known "good" device) with the tested one based on their remnant noise.

We apply this algorithm for detection of the Au (10⁻⁶ M) and Pd (10⁻⁶ M) traces relatively the background phosphate buffer. In order to detect the statistical significance of the desired particles presence the experiments were performed 100 times. This repetition allows to receive the maximal ranges of the CT(s)-1,2 in the given solute.

Initial curves are prepared by the following way. The scale (for convenience) was increased in 10⁷ times, then the mean curve was calculated and the remnants obtained after subtraction of the mean curve (corresponding to the most sensitive anode branch) was subtracted. Mathematically, this operation is expressed as

$$Md_s = y_s - \langle y \rangle, \langle y \rangle = \frac{1}{M} \sum_{s=1}^M y_s, \quad (1)$$

$$s = 1, 2, \dots, M.$$

Here the variable y_s ($s=1, 2, \dots, M$), (in our case the total number of measurements $M=100$) coincides with the corresponding VAG belonging to the selected anode branch. The corresponding two curves corresponding to the maximal (up) and minimal (dn) remnants for the background buffer are shown in Fig.3.

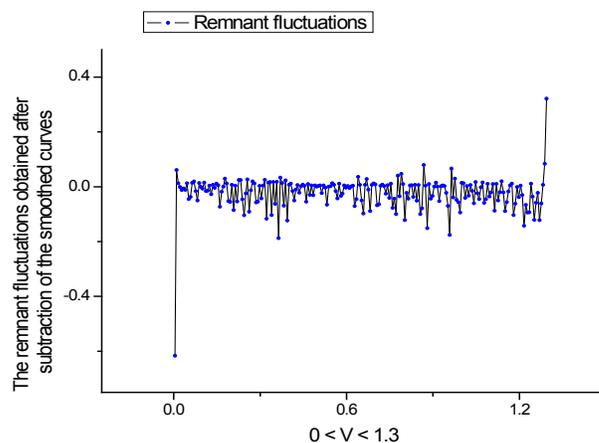


Figure 3: The remnant fluctuations obtained after subtraction of the corresponding smoothed curves. From all sampling including 100 measurements, the maximal fluctuations are chosen

In order to save place we show only the key figures demonstrating the effectiveness of the proposed method. These figures (Fig.4-Fig.8) explain this simple algorithm. Details are explained in captions to them. As one can see from this simple analysis the maximal

range of the background buffer is narrower in comparison with the corresponding ranges of the curves corresponding to the presence of the metal particles (Au and Pd).

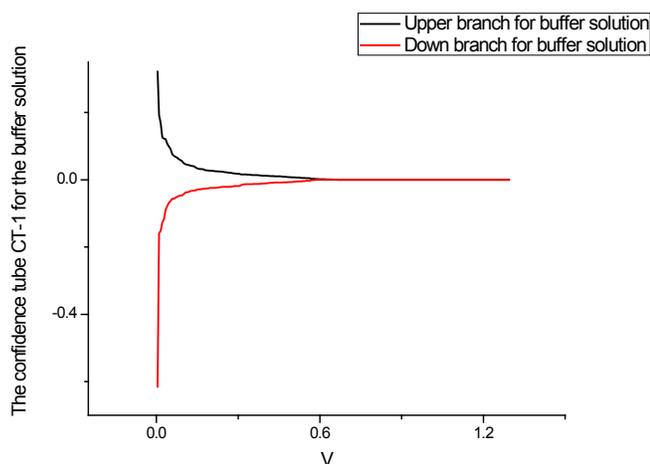


Figure 4: The sequences of the ranged amplitudes (SRAs) corresponding to the background/buffer solution. Other SRAs for metal particles cannot be shown here because of the strong difference of their ranges

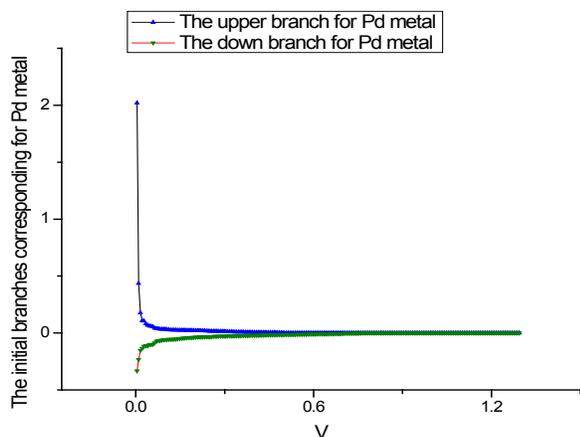


Figure 5: The sequences of the ranged amplitudes (SRAs) corresponding to the electrodes modified by Pd metal particles. We should show this range separately because of the strong differences of their amplitudes

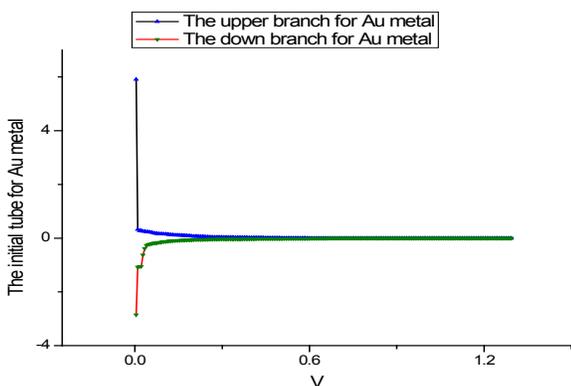


Figure 6: The sequences of the ranged amplitudes (SRAs) corresponding to the electrodes modified by Au metal particles.

Because of the strong differences between the amplitudes for two types of particles they cannot be shown together in one plot. The ranges for these three types of the tubes CT-1 are the following: $Rg(+,-) = 0.93613$ (buffer solute), 2.35498 (Pd), 8.76660 (Au).

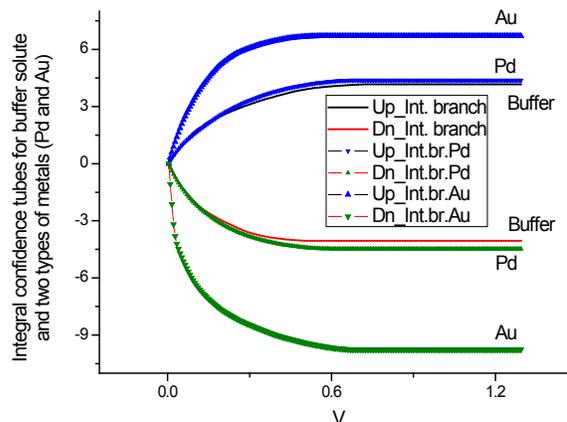


Figure 7: This key plot demonstrates the difference between the integral confidence tubes (CT-2), corresponding to the buffer solution (internal tube) and tubes for metal particles. Analysis of the plots shows that the metal particles for Au demonstrate more strong deviations in comparison of the CT-2 for Pd metal.

The values of the ranges $Jr(+,-)$ are the following: 8.21977 (buffer), 8.84757 (Pd) and 16.46097 (Au).

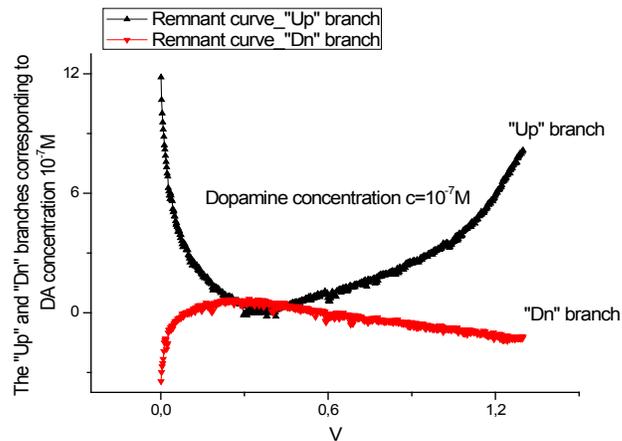


Figure 8: The "Up" (maximal values) and "Dn" (minimal values) curves for concentration of dopamine (DA $10^{-7}M$) with presence of Au ($10^{-6}M$). These differences are seen clearly only for the remnant curves that are defined by expression (1). The similar curves for DA concentration $c=10^{-8}M$ and Au ($10^{-6}M$) look similar and therefore they are omitted.

Electrooxidation of dopamine on the modified electrodes
At the process of DA electro-oxidation on the Au-GCE only one peak is registered on the anode branch at $E=0.50$ V Fig.9) due to reaction described in [14].

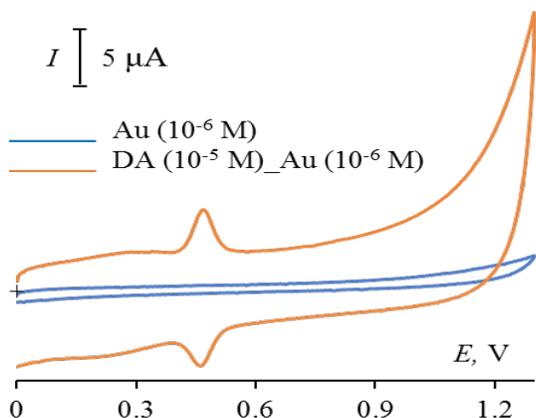


Figure 9: Cyclic voltammograms obtained at Au-GCE (at $t_e = 5$ s) in the absence (1) and in the presence (2) of 1×10^{-6} M dopamine on background phosphate buffer pH 6.86

The linear dependence of the current peak against the DA concentration is observed in the interval 5×10^{-3} до 5×10^{-7} M. Analyzing the peak current values (i_p) against the applied potential velocity (v) we found that with increasing of the value v the peak current height decreases. The slope of the logarithmic dependence i_p vs v ($\Delta \lg i_p / \times \lg v$) equals 0.32. It gives a ground to state that in this case we deal with a process complicated by a chemical reaction. Therefore, the DA oxidation process on Pd-GCE one can explain from the electrocatalysis positions. The background current fluctuations change the limits of a possible traces detection.

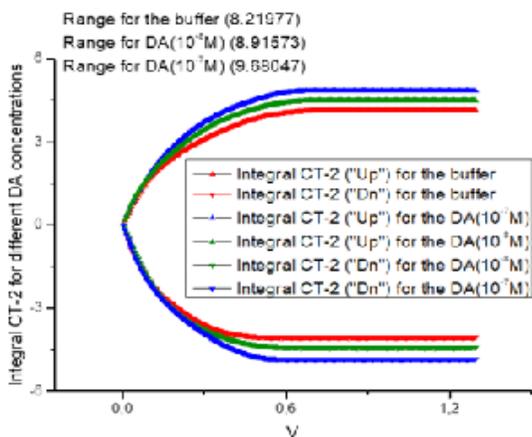


Figure 10: The key figure corresponding for the dopamine traces detection in presence of the Au particles in concentration $c = 10^{-6}$ M. As one can see from this figure the proposed method definitely detects the presence of dopamine in concentrations (10^{-7} , 10^{-8} M). The experiment with DA 10^{-9} M gives the range close to the buffer range and, therefore, it cannot be detected. The integral confidence tubes are more reliable in comparison with tubes depicted in Figs 4 and 5 because the outliers presented on the ends of the CT-1 are smoothed

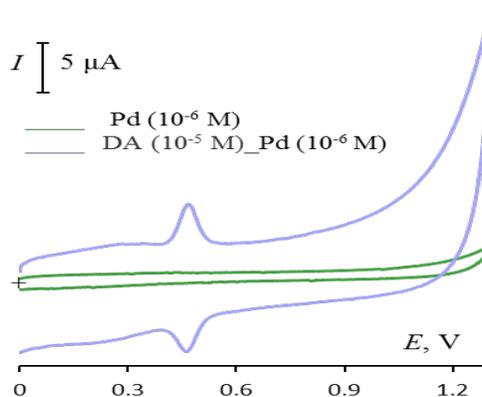


Figure 11: Cyclic voltammograms obtained at Pd-GCE (at $t_e = 5$ s) in the absence (1) and in the presence (2) of 1×10^{-6} M dopamine on background of 0.1 M solution of H_2SO_4

As it follows from the analysis of the Fig.8 and Fig.10 the proposed method detects the small DA concentrations (10^{-7} , 10^{-8} M). The experiment with DA (10^{-9} M) gives the range close to the buffer range and, therefore, it cannot be detected. The integral confidence tubes are more reliable in comparison with tubes depicted in Fig.5 and Fig.6 because the outliers presented on the ends of the CT-1 are smoothed. Therefore, the usage of integral tubes is more preferable. The CT-1 can be used in cases when the outliers presented in the ends are small or can be removed. We deliberately kept them in order to demonstrate a potential reader this peculiarity.

Using the same algorithm, we applied it for detection of DA in concentrations (10^{-7} , 10^{-8} M). Similar results were obtained at DA oxidation on the Pd-GCE. On the anode branch we observe one step only (Fig.11). Its height depends on the DA concentration and it is controlled by the kinetics of the corresponding chemical reaction. The potential of DA oxidation peak maximum at $E = 0.50$ V corresponds to the modifier potential. Hence, reduction of overvoltage of DA oxidation is 200 mV. Therefore, the application of the proposed mathematical method allows applying new algorithm for chemical data treatment and extract the deterministic information from fluctuations decreasing the level of the DA detection up to 10^{-8} M.

The obtained results can present an interest for the catalyst chemistry in general and different technologies associated with modification of electrode surfaces, in particular.

New mathematical approach related to evaluation of the deterministic/ useful analytic signal, which can be "hidden" in fluctuations of the background electrolyte, allows to receive useful information about the sensor response in the presence of the uncontrolled mixtures creating electrochemical noise.

The proposed mathematical method associated with treatment of fluctuation currents of the background electrolyte can be used in detection of metallic particles traces on the electrode surfaces. It enables to display potentially the catalytic properties in conditions of organic voltamperometry. These extremely low concentrations of metallic particles do not have practically own response, however, the proposed method can detect their presence.

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