Conference paper

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Interrupted amperometry: the new possibilities in electrochemical measurements

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Abstract: Interrupted amperometry is a new highly sensitive method for diffusion current measuring. The main feature of the proposed technique is the use of capacitive current as the analytical signal together with the faradaic current. The conventional electrical circuit for amperometric measurements is complemented by a switcher that enables periodical interruption of the circuit. The technique was successfully applied for direct amperometric determination of lead, cadmium and iron ions, phenol and hydroquinone; for determination of dichromate ion via titration; for determination of dissolved oxygen in water by Clark-type sensor. In all the mentioned cases the achieved values of analytical characteristics are significantly better than for conventional amperometric methods. There are limitations and perspectives of the proposed technique considered.

Keywords: amperometry; analytical chemistry; aqueous solutions; chemical sensors; electrochemistry; electrodes; heavy metals; iron; Mendeleev XX; oxygen; phenol; sensitivity; trace elements.

Introduction

Amperometry and voltammetry are powerful tools of analytical chemistry, including electrochemical sensors [1–4], detection in chromatography [5–7], flow analysis [8–10], titration [11, 12], etc. Sensitivity of these methods is defined by the signal-to-noise ratio [13, 14]. Traditionally, the signal is associated with the diffusion controlled faradaic current produced by the charge transfer reaction of the analyte. The residual current, consisting of the capacitance or the charging current and the faradaic currents caused by the reduction or oxidation of electroactive impurities, are conventionally referred to the noise. The capacitance current appears to be the main interference. Thus, the increase in sensitivity in voltammetry and amperometry is usually achieved by reduce of the capacitance current or by magnification of the faradaic current. One can distinguish two general approaches to enhancing the signal-to-noise ratio – mathematical and instrumental methods (see Table 1).

Mathematical techniques operate with experimentally collected data, and effectively eliminate noiselike signals thus improving sensitivity and resolution. However, these methods do not improve the analytical signal physically. Moreover, in some cases signal processing can result in the loss of a useful part of the current. Separation of the capacitance and faradaic currents is realized in instrumental methods based

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Table 1: Main approaches to enhancing the signal-to-noise ratio.

Instrumental methods
 Time-selective current measurements: Pulse voltammetry [26–28] Differential pulse voltammetry [29, 30] Square-wave voltammetry [31–33] Phase-selective current measurements: Alternating current [34–37], including sinusoidal voltammetry [38–40] Stripping techniques [41–45]

on time- and phase-selective current measurements. Various stripping techniques provide great sensitivity because of the faradaic current magnification due to analyte preconcentration.

A fundamentally new approach to enhancing the signal-to-noise ratio in amperometry was first proposed by Moshkin and Khustenko in 2012 [46]. The idea is to include the capacitive current in the analytically useful part of the signal together with the faradaic current. Technically this is realized by adding a switcher to the conventional electrical circuit for amperometric measurements. That way the measuring circuit is periodically interrupted and the structure of the analytical signal becomes more complicated. The new method was called "interrupted amperometry" (IA) [47]. Here we present a short review of its analytical applications based on our recent studies and discuss its possibilities for analytical chemistry.

The principle of interrupted amperometry

The theoretical consideration of interrupted amperometry as well as the design of the original home-made potentiostat "ComPot" were given in detail in our previous work [47]. Here we present only the key points of the theory that are essential for understanding the principle of the method under consideration. The scheme of the measuring electrical circuit for interrupted amperometry is presented on Fig. 1.

We assume that the measurement is performed under stationary diffusion of a depolarizer and the polarizing potential difference is constant and belongs to the limiting current potential region, i.e. the diffusion flow to the working electrode is constant. In this case the circuit part consisting of the serially connected charge transfer resistance (R) and the Warburg impedance (W) can be replaced by the value of direct current:

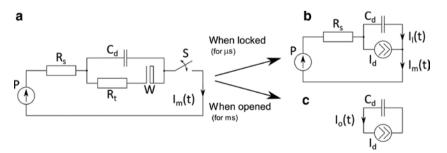


Fig. 1: (a) General scheme of the measuring electrical circuit for interrupted amperometry. (b) Simplified circuit for the locked state. (c) Simplified circuit for the opened state. P, potentiostat providing the polarizing voltage; Re, total ohmic resistance of electrochemical cell; R., charge transfer resistance; C_a , double layer capacity; W, Warburg impedance; S, switcher; $I_m(t)$, measured current; I_n direct current of electrochemical reaction; $I_n(t)$, current emerging in the outer circuit path at the locked state; $I_{o}(t)$, double layer discharging current at the opened state.

$$I_d = nFA \frac{D}{\delta} C_x^0, \tag{1}$$

where n is the number of electrons, involved in electrochemical reaction; F is the Faraday constant; A is the surface area of the working electrode; D is the diffusion coefficient; δ is the thickness of the Nernst diffusion layer; C_{\circ}° is the bulk concentration of the analyte.

The switcher (S) locks the circuit for the period of time t_1 (μ s) and then opens the circuit for the period of time t_2 (μ s). The sum of these times is called "the period of switching":

$$T = t_l + t_o. (2)$$

The switching is performed during the entire experiment. After several first periods the full charging of the capacitor (C_d) is achieved. Then at every locking of the circuit the capacitor is recharged by the current $I_i(t)$, that emerges in the outer circuit path. At every opening of the circuit the double layer (DL) partially discharges. This process produces the current $I_o(t)$ that supports the current of electrochemical reaction. Recharging and discharging of the capacitor are repeated until a stationary state is achieved. This state is characterized by the current $I_m(t)$ that can be measured in the outer circuit path when the switcher locks the circuit. The average value of $I_m(t)$ is used as analytical signal and is proportional to the diffusion current produced by the analyte discharge:

$$I_m = \frac{T}{t_l} I_d. (3)$$

The T/t_1 ratio serves as an amplification factor and usually its value is of several orders. However, this coefficient practically amplifies not only the analytically useful diffusion current I_d , but also all the noise currents I_i produced by interfering processes. Therefore, the expression (3) should be written as follows:

$$I_m = \frac{T}{t_i} (I_d + \sum I_i), \tag{4}$$

where I_i are interfering currents depending on the experimental conditions and set up.

Experimental

Electrochemical measurements were performed using a home-built computer controlled potentiostat "ComPot" that allows to work in direct-current and interrupted-current modes. High-performance potentiostat provides transition time of not more than 10 μ s. The device offers the opportunity to compensate of the initial current.

All electrodes were supplied by Metrohm (Switzerland), unless otherwise is indicated in the text below. Measurements were carried out at room temperature in a Faraday cage. The reagents used were of analytical grade. All aqueous solutions were prepared using deionized water of resistivity 18.2 M Ω cm (25 °C, D-301 deionizer, Akvilon, Russia).

Ideal case: the determination of cadmium and lead at the static mercury drop electrode by direct IA

Mercury electrodes are often referred to as the "ideal" working electrodes [14]. In case of an ideally polarized electrode the applied charge is fully utilized to DL charging in a wide potential range. Usually electrochemi-

cal reactions occurring at mercury electrodes are not affected by side reactions. Thus, the expression for the measured current (4) in case of mercury electrode usage as a working electrode for IA measurements can be transformed into a rather simple form:

$$I_{m} = \frac{T}{t_{l}} (I_{d} + I_{imp} + I_{tr}), \tag{5}$$

where $I_{\rm imp}$ is the current caused by the reduction or oxidation of electroactive impurities, $I_{\rm tr}$ is the transition current corresponding to the process of potential setting after switching. If the transition time of potentiostat is at least ten times less than the locking time, the value of $I_{\rm tr}$ becomes negligible. The potentiostat used for IA measurements provides the transition time of not more than 10 μ s. So, the latter summand in equation (5) can be neglected. Therefore, the interfering (or noise) current occurs only because of the presence of electroactive impurities in case of mercury electrode. That's why the first analytical experiments with interrupted amperometry were performed at the fine static mercury drop electrode (SMDE). The choice of model analytes, namely cadmium and lead, is explained by their high toxicity and abundance [49, 50], and hence, the high relevance of their determination in environmental analytical chemistry.

Cadmium (II) and lead (II) ions were determined in aqueous solutions via interrupted amperometry in direct mode. The measurements were carried out in a three-electrode cell of VA Computrace analyzer (Metrohm, Switzerland) attached to the potentiostat "ComPot". The cell consisted of the static mercury drop working electrode (drop size ca. 0.6 mm^2), silver/silver chloride reference electrode with double junction and platinum counter electrode. Stirring was provided by a mechanical rod stirrer with the speed of 1600 rpm. Supporting electrolyte was acetate buffer solution with pH 5. The following timing parameters were used: locking time t_l = 100 μ s, opening time t_o = 300 ms. Amperometric measurements were conducted at the potential belonging to the limiting current potential region. Preliminary voltammetric experiments showed that the proper detection potential for cadmium (II) ions is -0.60 V (vs. silver/silver chloride electrode), for lead (II) ions -0.40 V.

Ultrasensitive electrochemical methods of analysis require extra attention to the presence of even the smallest amounts of electroactive impurities, primarily dissolved oxygen. In order to study the influence of oxygen presence on IA measurements amperograms were recorded with additions of deionized water saturated by atmospheric oxygen (black line of Fig. 2) and with additions of the standard solution containing cadmium (II) ions (red line of Fig. 2).

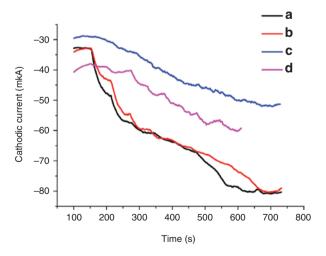


Fig. 2: The influence of dissolved oxygen presence on IA measurements. a (black) – Amperogram obtained with additions of deionized water saturated by atmospheric oxygen. b (red) – Amperogram obtained with standard additions of Cd²⁺ solution. c (blue) – Amperogram obtained with standard additions of deoxygenated Cd²⁺ solution. d (pink) – Amperogram obtained with standard additions of deoxygenated Cd²⁺ solution. The area above the solution was blown with argon during the measurement.

As it can be seen in Fig. 2, the obtained amperograms have similar forms. This means that the standard solution of Cd²⁺ needs to be released from oxygen. Therefore, all standard solutions used for direct IA measurements were bubbled with ultrapure argon for at least 40 min prior to their use.

Amperogram obtained with additions of the standard Cd²⁺ solution after the described procedure was recorded in a more sensitive current range (see the blue "c" line of Fig. 2). However, the continuous current drift does not allow us to identify stairs corresponding to the additions of the analyte. This stable current decrease was caused by oxygen present in the area above the solution in the measuring cell. In order to eliminate this interference the described area was blown by ultrapure argon during direct IA measurements. As a result, amperogram was obtained with well-defined stairs each corresponding to the standard addition of Cd²⁺ ions (the pink "d" line of Fig. 2).

The analytical possibilities of the proposed technique for determination of lead and cadmium at SMDE were evaluated. It was found that the dependence of the measured current on Cd²⁺ concentration is linear in the range from 1 till 200 nM ($y = 10^9x + 17.599$, $r^2 = 0.998$) and for Pb²⁺ ions – from 5 till 200 nM $(y=2*10^9x+9.2191, r^2=0.995)$. Practical limits of detection (LOD), calculated as three times the signal to noise ratio, are 0.26 nM and 0.79 nM for cadmium (II) and lead (II) ions respectively. These LOD values are typical for the present-day stripping techniques utilizing amalgam concentration [51], but are quite remarkable for direct amperometry.

General case: interrupted amperometry using solid electrodes

The use of mercury electrodes in the practice of analytical chemistry is often associated with some experimental manipulation difficulties. That is why it is important to consider the application of solid working electrodes for IA measurements.

Solid electrodes are characterized by the significantly narrower region of the ideal polarizability. In this case the applied charge is utilized not only for DL charging but also for various processes associated with the charge transfer. In general case the residual current is related to all the processes occurring at the electrode-solution interface. The following processes can appear when we use solid electrodes: electrochemical dissolution of electrode material; formation of oxide films; adsorption of solvent components (oxygen and hydrogen for water); electrochemical instability of solvents (release of oxygen in the anodic region and release of hydrogen in the cathodic region for water). Consequently, the sensitivity of IA measurements is influenced by the magnitude of the current associated with non-ideal polarizability of working electrode and the current caused by reduction or oxidation of electroactive impurities, since current types are not dependent on the analyte concentration, but are dependent on the gain value. That is why the expression (4) for the measured current in general case can be presented as following:

$$I_m = \frac{T}{t_l} (I_d + I_{imp} + I_{nonid}), \tag{6}$$

where I_{nonid} is the current associated with various processes occurring on the electrode surface and responsible for its non-ideal polarizability. Therefore, when planning an IA experiment it is important to select the material of the working electrode that is characterized by the minimum value of background current in the area of analyte's detection potential. We used solid electrodes for the direct IA determination of hydroquinone, phenol and iron.

The determination of hydroquinone and phenol

The determination of hydroquinone was carried out in a three-electrode cell using phosphate buffer solution (PBS) with pH 6.9 as a supporting electrolyte. The reference electrode was silver/silver chloride electrode and the auxiliary electrode was a glassy carbon crucible. The following electrodes were considered as working: rotating disk electrodes made of gold, platinum, and glassy carbon ($S = 0.78 \text{ mm}^2$) and polymeric polyethylene- and carbon-based composite electrode (Tom'analit, Tomsk) ($S = 1.96 \text{ mm}^2$). In order to choose the optimum material of the working electrode, dependences of current density on potential were registered using all of the mentioned electrodes. The obtained results are summarized in Fig. 3.

These voltammograms were registered at the stepwise potential sweep. The interrupted mode of the measurements requires the presence of at least one period of switching during a step. Consequently, the sweep rate for the specified period of switching (100 ms/100 µs) should not exceed 4 mV/s. In order to obtain sufficiently detailed voltammograms we used 1 mV/s sweep rate. Three regions (roughly indicated by two vertical solid lines on Fig. 3) can be distinguished for the four presented graphs. In the first region, a sharp decrease and then an increase in current is observed due to the charging of DL capacitance and also to the attainment of the initial potential value. The second region is a plateau and hence it corresponds to the working region of the electrode. In the third region a smooth but considerable increase in the background current is likely associated either with electrochemical decomposition of the solvent or with electrochemical corrosion of the working electrode material. We compared the values of current density in the limiting current potential range (from 0.5 till 0.9 V) of hydroquinone. As it can be found on Fig. 3 the least residual current related to non-ideal polarizability of electrode is demonstrated by the composite electrode. Consequently, the use of this electrode can provide more sensitive determination as compared with the other electrodes under study. The polymeric carbon-based electrode was, thus, selected as the optimum for quantitive hydroquinone determination. The analogous experiment described in [48] was conducted using a 1% solution of sulfuric acid as a supporting electrolyte for selecting the most suitable electrode for phenol determination. It was found that in this case, the composite electrode is the most appropriate too.

Analytical characteristics of direct IA for the quantitive determination of hydroquinone and phenol using the polymeric carbon-based composite electrode were evaluated. It was shown that the dependence of the measured current on phenol concentration is linear in the range from 0.5 till 3 μ M, and from 0.1 till 5 μ M for hydroquinone. Limits of detection calculated using the 3 σ -criterion were found to be 8.8 nM for phenol and 0.3 nM for hydroquinone. It should be noted that these LOD values are characteristic for amplification factor of 4000, i.e. for the specified period of switching. Sensitivity is defined by the slope of the linear region of calibration curve and reached the value of 76 nA/ μ M for phenol determination and 75 nA/ μ M for hydroquinone [48].

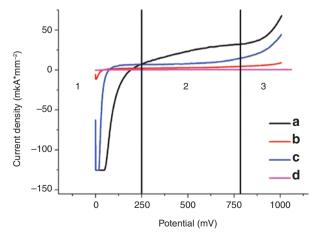


Fig. 3: Selection of the working electrode material for hydroquinone determination. Voltammograms were obtained using: a – platinum electrode; b – gold electrode; c – glassy carbon electrode; d – polymeric carbon-based composite electrode.

The determination of iron

The similar approach to the selection of the working electrode material was applied for the determination of iron. Cyclic voltammograms were registered using carbon and gold RDE of the same 2 mm diameter in blank supporting electrolyte solutions and in solutions containing Fe³⁺ ions. The obtained curves are shown in Fig. 4. If we compare the values of the residual current registered on blank voltammograms in the regions of limiting current, for example, at +0.1 V in case of carbon RDE (see the black "a" line on Fig. 4) and at +0.7 V in case of gold RDE (see the blue "c" line of Fig. 4), we can notice the difference of about one thousand times. On the one hand, this means that the preferable electrode for iron determination is carbon RDE. On the other hand, the used potentiostat is able to compensate of the initial current, thus, providing additional possibilities for sensitivity enhancing. Therefore, analytical characteristics were evaluated for iron determination at both carbon and gold RDEs.

Determination of iron (III) at a carbon rotating disk electrode (RDE) in aqueous solution by direct IA is described in [47]. It was found that the theoretical limit of detection calculated from the calibration plot is 3 nM. The calibration curve is linear in the whole investigated concentration range from 0.02 to 0.38 µM and gives a value of $1.22 \,\mu\text{A} \,\mu\text{M}^{-1}$ for the sensitivity. These promising characteristics were compared with the values obtained in conventional direct-current amperometry mode with other experimental conditions being the same: 0.2 μM and 0.81 nA μM⁻¹ for LOD and sensitivity, respectively. The accuracy verification of the proposed technique showed that it does not produce any significant systematic errors.

Similar experiment was performed at gold RDE as a working electrode for iron (III) determination. Silver/ silver chloride reference electrode and platinum counter electrode were used. Supporting electrolyte was 0.1 M HCl prepared by the dilution of concentrated ultrapure hydrochloric acid with deionized water. Detection potential was held at ± 0.70 V. Locking time was ± 100 μs and the period of switching was ± 300 ms. Calibration plot ($y = 10^9x + 36.947$, $r^2 = 0.9995$) obtained under stated conditions by the method of standard additions was found to be linear in the concentration range from 0.01 till 1 μM of Fe³⁺ ion. The practical LOD reached the value of 2.5 nM, which is very close to the theoretical LOD obtained at carbon RDE. The proposed technique was tested on real samples of Baltic Sea bottom water. After acidic microwave-assisted sample preparation these 11 water samples were analyzed by IA and electrothermal atomic absorption spectroscopy (ETAAS) using AA-7000 spectrophotometer (Shimadzu). Results obtained by these two methods are presented in Table 2 and show good agreement with each other. This means that direct IA can be successfully applied in practical analytical chemistry.

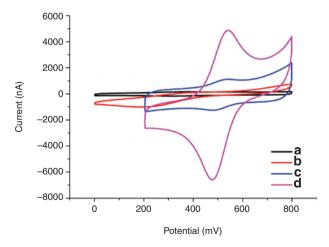


Fig. 4: Selection of the working electrode material for iron determination. a - Cyclic voltammogram obtained using a carbon RDE in 0.1 M nitric acid as supporting electrolyte without any additions, b - voltammogram registered after a standard addition of Fe (III) ion. c - Background voltammogram obtained using gold RDE in 0.1 M hydrochloric acid, d - voltammogram registered after a standard addition of Fe (III) ion. The sweep rate in all cases is 50 mV/s.

Sample #	ETAAS results, (C±ΔC) μg L ⁻¹	IA results, (C±ΔC) μg L ⁻¹
LL3A	12.1±1.2	12.6±1.9
33F	18.5 ± 1.1	19.9 ± 5.3
LL5	12.0 ± 2.0	13.1 ± 1.8
6P	10.3 ± 2.4	9.9±3.1
NAR3	11.6 ± 1.8	11.0 ± 1.9
F42	9.8 ± 1.1	10.0 ± 2.0
LL9	11.6 ± 1.5	11.2 ± 1.4
GF6	17.1 ± 1.2	16.6 ± 0.5
10F	15.1 ± 0.8	13.7 ± 2.0
LL12	13.5 ± 1.7	15.1 ± 1.4
117	9.9+1.2	13.7+1.7

Table 2: Concentration (C) of Fe³⁺ ion determined by ETAAS and IA in the samples of Baltic Sea bottom water (n = 2, P = 0.95).

Interrupted amperometric titration: the determination of dichromate ion

In amperometric titration the influence of the working electrode material is not as significant as in direct amperometry, because the value of the measured current is of interest only as an indicator. The shape of titration curve depends on the role of electrochemically active substance, which can be analyte, titrant or their reaction product [14]. One of the assumptions made for theoretical consideration of IA in our previous work [47] stated that the concentration of a depolarizer is so low, that the current of electrochemical reaction is much lower than the DL charging current. This condition is easily fulfilled when an electrochemically inactive substance is titrated by electrochemically active titrant.

A well-known technique for determination of dichromate ions based on their reduction by iron (II) ions [52] was used as a model system in order to investigate the possibilities of IA in titration mode. The measuring electrochemical cell consisted of platinum RDE (diameter 2.0 mm, rotation speed 2000 rpm) as a working electrode, platinum rod as a counter electrode and a silver/silver chloride reference electrode. The potential was held at +1.0 V (vs. silver/silver chloride electrode) and amplification factor was 1000. A standard 0.01 M solution of ammonium iron (II) sulfate served as titrant. Both titrant and model analyte solutions were deoxygenated by argon prior to measurements.

The end point is found graphically as the point of intersection of the "residual current" line before the end point and of the anodic diffusion current line of the ferrous iron after the end point (see Fig. 5b). Preliminary studies showed that the acceptable value of the error ($\pm 0.7\%$) is achieved when the concentration of dichromate ion is not less than 1.68 μ M.

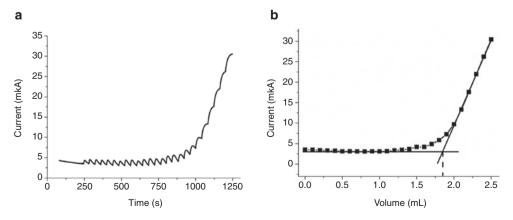


Fig. 5: Typical amperogram (a) and the corresponding titration curve (b) obtained with IA detection.

Using of direct interrupted amperometry in a Clark-type sensor

The use of direct IA for detection in electrochemical sensors is of particular interest. This approach was applied to determine concentration of dissolved oxygen in water by Clark-type sensor. The problem of the ultrasensitive determination of dissolved oxygen in high-purity aqueous media is topical, for example, in thermal and nuclear power industry [53]. Therefore, ultrapure water obtained by the ion-exchange deionization of distilled water, being in equilibrium with atmospheric air, was taken as a model sample to be analyzed. Changing the concentration of dissolved oxygen was achieved by adding fixed amounts of sodium sulfite. This procedure provided decrease in O, concentration to the required value due to a redox reaction. The experimental setup was assembled as follows. Two sensors were immersed in a 300 mL beaker filled with deionized water. The first was Clark-type oxygen sensor AKPM-02 ("Al'fa BASSENS" Company OOO, Russia) attached to "ComPot" potentiostat. The second sensor was a part of commercially produced MARK-302T oxygen meter ("VSOR" Company OOO, Russia) that was used as a reference device. The beaker was placed on a magnetic stirrer and covered with laboratory film "Parafilm" ("Pechiney Plastic Packaging") that did not allow oxygen inflow. Additionally, the area above the water in the beaker was blown with ultrapure argon. Amplification factor of 1000 was used in direct IA-mode and detection potential was -0.7 V. After a constant response was achieved from both MARK-302T oxygen meter and "ComPot" potentiostat, we started to lower the concentration of dissolved oxygen by successively adding 10 mg portions of sodium sulfite. As a result a chronoamperogram presented on Fig. 6a was registered and a calibration plot (see Fig. 6b) was obtained.

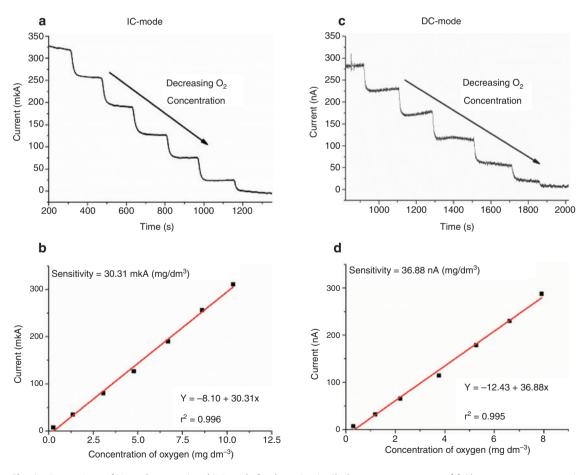


Fig. 6: Comparison of IA- and conventional DC-mode for detection in Clark-type oxygen sensor. (a) Chronoamperogram registered in IA mode. (b) Calibration plot obtained for IA mode. (c) Chronoamperogram registered in DC mode. (d) Calibration plot obtained for DC mode.

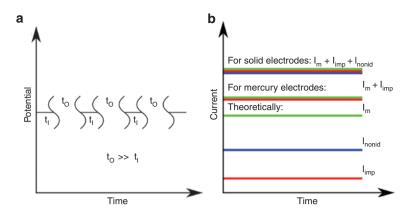


Fig. 7: The principle of interrupted amperometry: excitation factor (a) and analytical signal (b).

The slope of the calibration curve gave a value of $30.31 \,\mu\text{A}/(\text{mg/dm}^3)$ for the sensitivity of IA technique. The similar experiment was carried out in conventional DC amperometric mode in order to compare the sensitivity of the proposed technique with this of a common method (see Fig. 6c and d). It was found that the use of IA mode for detection in Clark oxygen sensor provides a significant gain in sensitivity. The proposed technique is approximately a thousand times more sensitive than conventional one.

Conclusions and perspectives

The principle of interrupted amperometry can be briefly represented by depicting the scheme of excitation factor (Fig. 7a) and the structure of analytical signal (Fig. 7b). As it follows from Fig. 7b, sensitivity of IA measurements depends on the material of the working electrode and on the amount of electroactive impurities.

Thus, the development of the sensitive and selective IA methodology requires the selection of the appropriate supporting electrolyte solution and of the optimum working electrode material, just like it is in conventional amperometry.

Interrupted amperometry provides significantly better analytical characteristics as compared with those typical for conventional amperometric techniques. This is confirmed by the obtained LOD values in direct IA mode for cadmium (0.26 nM) and lead (0.79 nM) divalent ions at the static mercury drop electrode, for phenol (8.8 nM) and hydroquinone (31 nM) at the polymeric carbon-based electrode, and for iron (III) at the carbon RDE (3 nM) and at the gold RDE (2.5 nM). The lowest concentration of dichromate ion estimated by IA titration was 1.68 µM with the error of 0.7 %. The sensitivity of the Clark-type sensor with IA detection of dissolved oxygen reached 30.31 μA/(mg/dm³). The mentioned experimental results show good prospects of the use of IA in analytical chemistry. In addition to expanding the range of analytes, we expect the future development of IA in its application for detection in HPLC, flow injection analysis and biosensors. Possibilities of IA for coulometry and electroanalysis with ultramicroelectrodes are also of great interest.

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