

# Electrocatalytic methods for determination of organic impurities and cations of certain metals in natural, drinking and sewage water

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Efficient methods of monitoring typical pollutants of natural, drinking and sewage water based on the high capacity of platinum for chemisorbing different organic substances and toxic metals have been developed. The methods are simple to use, lend themselves readily to automation and often allow determination of impurities in amounts not detectable by other methods.

## 1. Introduction

One of the vital problems of environmental protection is monitoring of the pollution level of water resources. Increase in the number of water reservoirs into which industrial effluents are discharged emphasizes the urgency of the automation of water analysis systems.

The components that are most difficult to determine in natural and sewage water analysis are organic impurities. Analysis of the organic substance content develops in two directions. The first direction involves development of methods for determining individual compounds and establishing the limits of maximum admissible concentrations of different substances. At present these limits have been established for over 500 organic substances [1, 2]; their determination is a matter of great complexity. The second direction is the development of general water pollution indexes and of methods for determination of the overall content of organic impurities. To estimate this content methods based on measuring the oxidizability of the sample are widely used [3, 4]. The values are expressed in  $\text{mg O}_2 \text{ l}^{-1}$  (COD) and are often used as a water purity index. If this value exceeds  $12 \text{ mg O}_2 \text{ l}^{-1}$ , the water is unsuitable for use as drinking water [5].

Depending on the oxidant used, permanganate and bichromate oxidizabilities are distinguished. Not all organic substances are oxidized by permanganate; bichromate in a concentrated sulphuric acid solution is a stronger oxidant. When water samples are boiled in this solution for 2-3 h in the presence of silver salts the degree of oxidation of organic pollutants is close to 100%. This method does not require any special equipment, but it has a low sensitivity, is time consuming and not fit for use in automatic water monitoring systems.

For control of water purity the spectrophotometric method can be used, based on direct measurement of the optical density of water in the UV spectral region at the wavelengths 230-254 nm. This method is widely used for determining the content of organic impurities in natural water [6]. Automatic analysers have been developed on this basis determining the organic

substance concentration in the range  $5-500 \text{ mg l}^{-1}$  within an accuracy of 5%.

At present, however, methods for determining the total organic carbon (TOC) are most widely used. These methods include two groups of operations: combustion or oxidation of organic substance to carbon dioxide and subsequent determination of its amount. High-temperature oxidation of a water sample is carried out in a quartz tube with a platinum catalyst heated to  $950^\circ \text{C}$  [7]. The evolving  $\text{CO}_2$  is determined by IR spectroscopy or chromatography. On the basis of this method, some firms have devised up-to-date models of these analysers which feature a very high sensitivity (50 p.p.b.), fast operation (analysis time 2-4 min) and computer automation of operations, data processing and storage.

Some modern analysers utilize low-temperature catalytic oxidation of organic substances in a water sample under the action of ultraviolet radiation using the method described in [8], followed by IR spectroscopic determination of  $\text{CO}_2$ .

All these analysers are costly, highly complex, bulky and require expert handling.

Simpler analysers are described in [9]. Therein water samples undergo oxidation with a sulphur-chromium mixture, followed by a coulometric determination of  $\text{CO}_2$  formed. The sensitivity of this method with respect to TOC is  $0.1 \text{ mg l}^{-1}$ , the accuracy at  $2 \text{ mg l}^{-1}$  is  $\pm 5\%$ , the range of measurement is  $0.3-1000 \text{ mg l}^{-1}$ , the analysis time being 90 min.

The present communication is concerned with the development of electrocatalytic methods for determination of organic impurities which are similar to voltammetry with accumulation widely used for analysis of the content of heavy metals [10-14].

## 2. Electrochemical methods of determination of total organic carbon in water

### 2.1. Hydrogen adsorption decrease method

This method is based on determining the poisoning of

a platinum microelectrode due to the high adsorptivity of platinum.

The degree of poisoning of a platinum electrode is determined from the decrease in hydrogen adsorption measured in the course of application of a fast potentiodynamic cathodic pulse in the potential range 0.4–0.0 V (all potentials are referred to the reversible hydrogen electrode in the same solution). This method of the so-called 'adsorption substitution' was formerly widely used for investigation of the adsorption of various organic substances and metal cations [15–24] and as a criterion of purity of supporting electrolyte [17, 20]. The employment of a similar method for analytical purposes based on the influence of adsorbed organic impurities on the double layer capacitance of platinum electrode was first suggested in [25].

Measurements are generally performed in a conventional three-electrode cell, 10 cm<sup>3</sup> in volume at room temperature (20 ± 2°C). A platinum wire 0.5 mm in diameter and 2–3 mm long serves as a working electrode and a platinum gauze 1 cm<sup>2</sup> in area as an auxiliary electrode. As reference electrode in acid solutions it is possible to use a mercuric sulphate electrode.

For adsorption measurements the charge necessary for adsorption of a monolayer of hydrogen atoms on the electrode is measured at first in a pure supporting electrolyte solution (0.5 M H<sub>2</sub>SO<sub>4</sub>) ( $Q_0^H$ ) [17] (Fig. 1). Next a sample of the test solution is added. After the adsorption equilibrium is reached one measures the charge needed for hydrogen adsorption on the sites of platinum surface free of the adsorbed organic substances ( $Q_R^H$ ). The coverage of the platinum surface with adsorbed substance  $\theta'_R$  is determined from the relative decrease in hydrogen adsorption. The value of the coverage in the range of medium coverages (0.1 <  $\theta'_R$  < 0.9) depends linearly on the logarithm of adsorbate concentration [17–19, 26–28] (Temkin's isotherm).

$$\theta'_R = a + \frac{1}{f} \ln C \quad (1)$$

Due to the existence of this dependence, valid over a wide potential range, it is possible, by measuring electrode coverage, to determine the volume concentration of the adsorbate. In using this method for analysis it is not convenient in each determination to make a comparison with the pure supporting electrolyte solution. Therefore in the analytical version all measurements are made directly in the solution containing the substance being determined (acidified with H<sub>2</sub>SO<sub>4</sub> up to the concentration 0.5 mol l<sup>-1</sup>) by means of a sequence of pulses which is introduced into the automatic device (Fig. 2) [29]. I – Preliminary preparation of the electrode consisting in its anodic-cathodic activation with square potential pulses from 1.6 to 0.0 V for 100 s. By this means previously adsorbed organic impurities, metal cations and supporting electrolyte anions are removed from the electrode surface. II – After a very short delay (0.2–0.8 s) during which the impurities present in

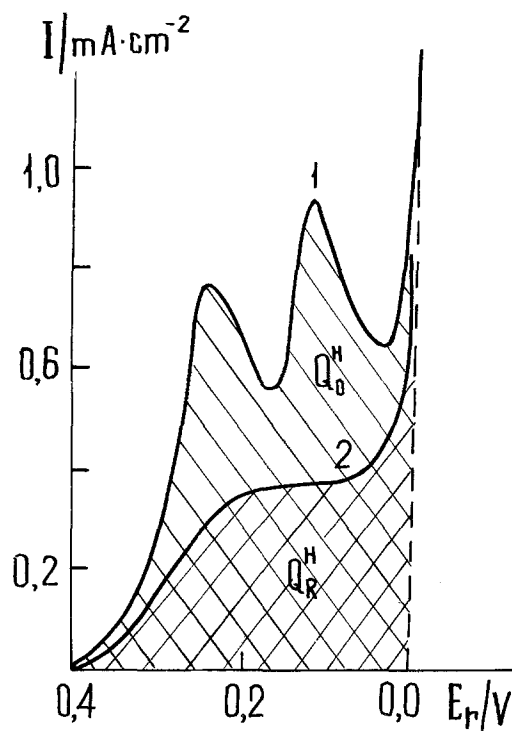


Fig. 1. Voltammetric curves of hydrogen adsorption on Pt electrode in pure solution 0.5 M H<sub>2</sub>SO<sub>4</sub> (1) and in the presence of organic impurities (2). Sweep rate 10 V s<sup>-1</sup>.

solution do not undergo adsorption, a linear potential sweep (10 V s<sup>-1</sup>) from 0.4 to 0.0 V is applied to the clean electrode surface during which the charge for hydrogen adsorption  $Q_0^H$  is recorded corresponding to the charge in supporting electrolyte (this was specially checked up in control tests). We shall call this measuring pulse the reference pulse. III – The adsorption step during which the electrode is maintained at the potential of maximum adsorption for the time necessary for the steady-state coverage to be formed or for a definite time necessary for the coverage to reach a reliably measurable value ( $\theta'_R > 0.1$ ). IV – The measuring pulse applied in the same potential range and at the same rate as the reference pulse during which the charge  $Q_R^H$  is measured which was expended in hydrogen adsorption on the part of the electrode surface free of adsorbed impurities. The charges determined during the reference and the measuring pulses are compared by means of a comparator, and from the relation

$$\theta'_R = \frac{Q_0^H - Q_R^H}{Q_0^H} \quad (2)$$

the value of the electrode coverage is calculated, which is displayed in digital form.

## 2.2. Potential decrease method

This method is a version of the method widely used previously [26, 30–32] in investigation of the mechanism of adsorption, dehydrogenation and interaction with the oxidized platinum surface of alcohols, aldehydes and carboxylic acids. In the analytical version a solid electrolyte cell is used, a cation-

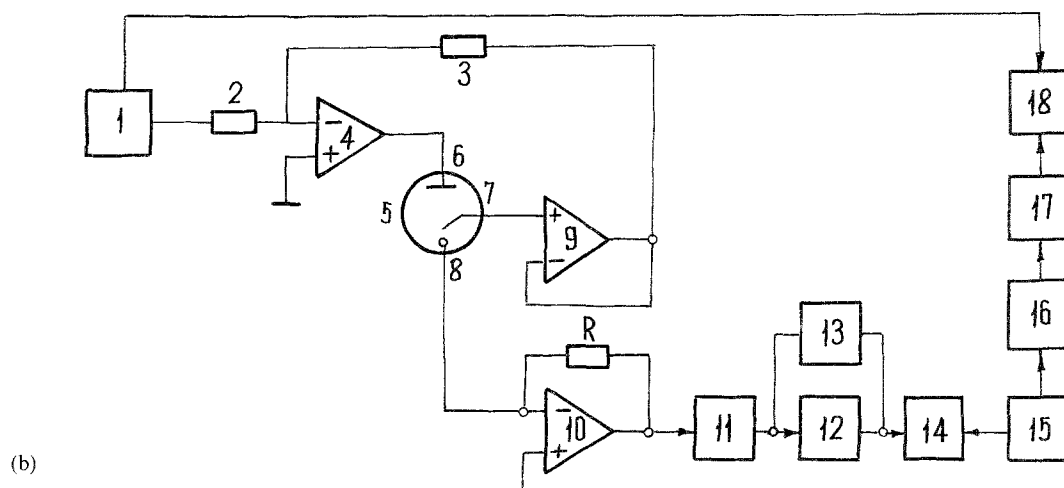
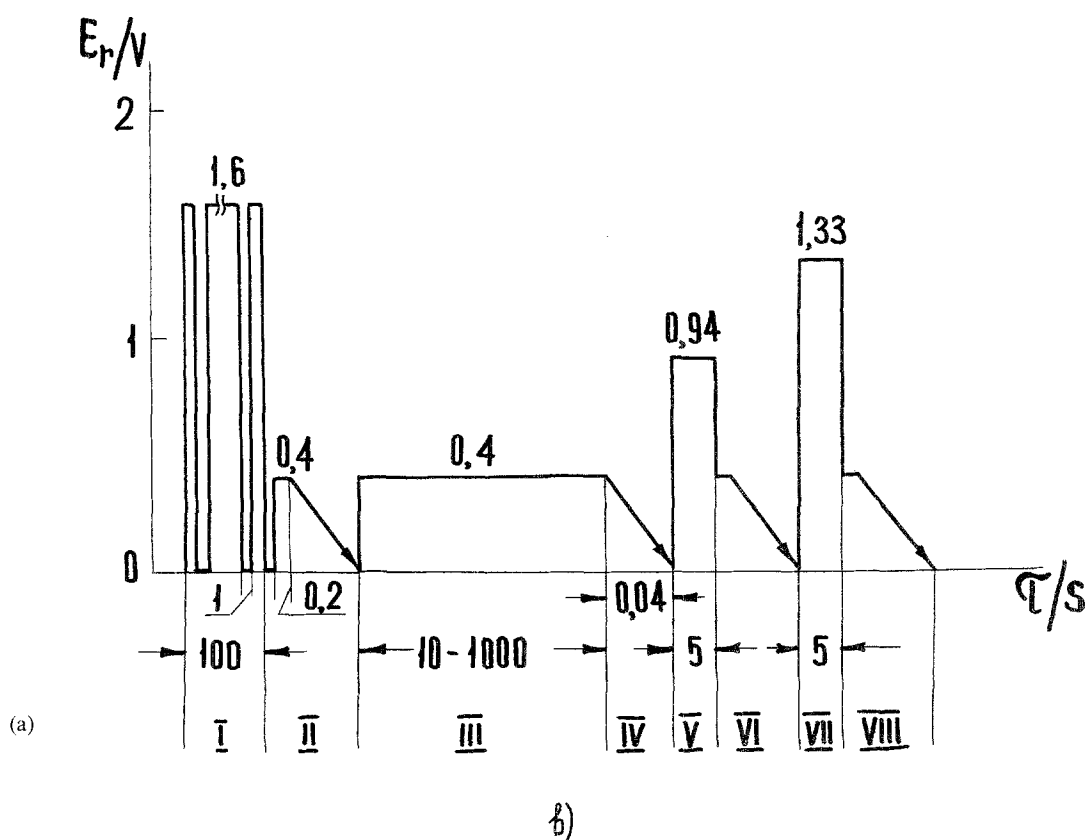


Fig. 2. (a) Scheme of the sequence of potentiodynamic pulses used in automatic analyser (explained in text) and (b) block diagram of the device: 1, programmer; 2, 3, scale resistors; 4, regulator-amplifier; 5, electrochemical cell; 6, auxiliary electrode; 7, reference electrode; 8, working electrode; 9, coupling amplifier; 10, direct-current amplifier; 11, 13, commutator; 12, integrating amplifier; 14, comparator; 15, digital attenuator; 16, digital-to-analog converter with memory; 17, state decoder; 18, digital dynamic indicator.

exchange polymer membrane (of Nafion type), 2 cm<sup>2</sup> in area, serving as electrolyte. On one side of the membrane platinum black is applied by a special process [33] (working electrode) and on the other side palladium black (serving as auxiliary and reference electrodes simultaneously) is applied. The auxiliary electrode is charged with cathodic current at regular intervals, so that its potential is held constant ( $\sim 0.05$  V). Platinum gauzes, closely pressed against the membrane over the blacks applied to the surface, serve as current collectors. Such a compact cell can be immersed in a water flow.

The method consists essentially of the following: the measuring platinum electrode is charged to a certain

potential in the oxygen adsorption range (1.0–1.5 V), whereupon the polarization circuit is broken. The organic substances present in solution interact with platinum surface oxides and as a result the potential shifts in the cathodic direction.

At first the  $E/\tau$  curve shows a sharp potential drop down to the potential of the beginning of the reduction of platinum surface oxide followed by the plateau of surface oxide reduction. The same amount of oxide being formed each time, the length of  $\tau$  of this plateau is the less the more organic impurities are present in solution and the stronger reductants they are. It should be noted that the rate of potential decrease depends on the concentration of organic impurities in

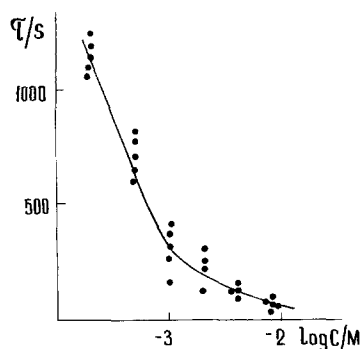


Fig. 3. Dependence of the electrode potential decrease time (from 1.4 to 0.94 V) on ethyl alcohol concentration in water.

solution for both sections of the  $E/\tau$  curve, so that any one of them, as found convenient, may be used for detection of organic impurities. For illustration, Fig. 3 shows the dependence of the time of potential drop from 1.4 to 0.94 V as a function of ethyl alcohol concentration in solution. The minimal concentration determinable by this method is  $5 \text{ mg l}^{-1}$ ; the error is 15–17%.

### 2.3. The method of oxidation under galvanostatic conditions

Like the preceding one, this method is suitable for determining only oxidizable organic impurities [15, 16]. The electrochemical cell represents a sensor of the same type as in the preceding method, but in place of the Pt and Pd blacks, a smooth electrode in the form of a platinum wire 0.2–0.3 mm in diameter and 20 mm long is used.

Two versions of this method were proposed. In the first version the electrode is polarized with constant current  $0.1\text{--}10 \text{ mA cm}^{-2}$  and the time necessary for potential change within a certain range (from 0.0 to 1.5 V) is measured. This time is the greater the larger the content of organic impurities in solution. In the second version alternating square wave polarization of the same current density is used and the number of potential changes in the range indicated during a certain time (100 s) is determined. In this case the greater the content of impurities the less is the number of these potential changes [34].

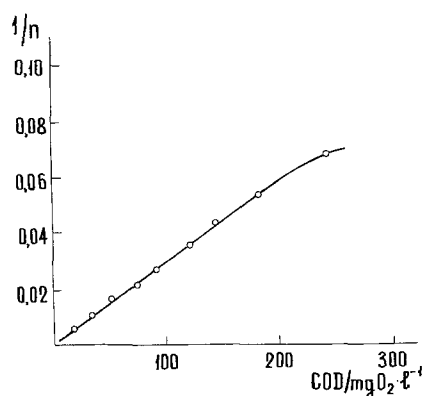


Fig. 4. Number of potential changes ( $n$ ) from 0.0 V to 1.5 V during 100 s vs concentration of organic impurities in water expressed in COD units.

Figure 4 shows the dependence of the reciprocal of the number of cycles ( $n$ ) of the potential change from 0.0 to 1.5 V in 100 s on the concentration of organic impurities in a model multicomponent solution (expressed in COD units). The dependence of the quantity  $1/n$  on concentration of organic impurities is linear. The minimal determinable concentration is 20 COD units.

The last two methods can be easily realized in automatic systems. Moreover, due to the use of a polymer membrane as electrolyte, such electrochemical sensors are very compact and can be located directly in the test water flow. The results obtained by these methods, however, are unsatisfactory as to sensitivity and reproducibility. Possibly, this is associated with the polymer membrane whose properties are very sensitive to solution composition.

Of the electrochemical methods tested by us, the first method — decrease of hydrogen adsorption in the presence of adsorbed impurities — proved to be the most sensitive and stable one. All the results given below were obtained by this method.

### 3. Determination of the concentration of individual organic substances and cations of certain metals

Figures 5–7 give the dependences of electrode coverage on the concentration of some organic substances.

As can be seen, the dependence ( $I$ ) is observed over a wide concentration range. Thus, for example, for benzene the linear section of this dependence covers the range of the concentration change  $10^{-7}\text{--}10^{-4} \text{ mol l}^{-1}$ , for phenol  $10^{-6}\text{--}10^{-3} \text{ mol l}^{-1}$  and for ethanol  $5 \times 10^{-4}\text{--}10^{-1} \text{ mol l}^{-1}$ .

The dependences under consideration have similar slope values (coefficient  $f$  in Equation 1) typical of a platinum surface, but for different substances they differ in the values of the coefficient  $a$  characterizing the substance adsorbability. The adsorbability value of organic substances depends on electrode potential [26–28]. The maximum adsorption is usually observed in the potential range near 0.4 V. At this potential  $\text{CO}_2$  adsorption from carbonates contained in natural waters (due to interaction with adsorbed hydrogen) is excluded and the influence of the cations and anions undergoing adsorption is minimal. All the results described in the present study refer to this potential.

The experimental data available at present [26–28,

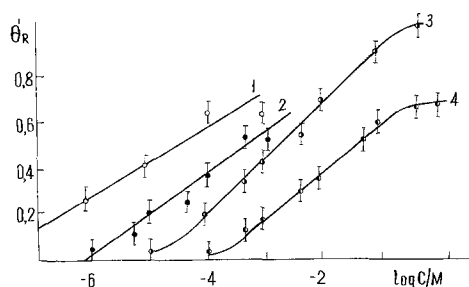


Fig. 5. Electrode coverage vs concentration of organic substances in  $0.5 \text{ M H}_2\text{SO}_4$ : 1, benzene; 2, phenol; 3, formaldehyde; 4, ethanol.  $E_{\text{ads}} = 0.4 \text{ V}$ ,  $\tau_{\text{ads}} = 100 \text{ s}$ .

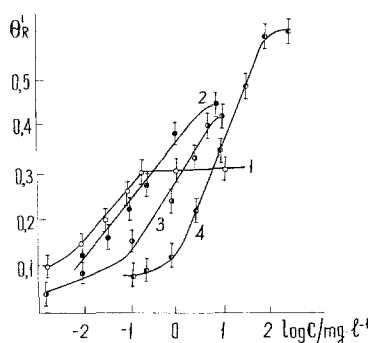


Fig. 6. Electrode coverage vs concentration of synthetic surfactants in 0.5 M  $H_2SO_4$ : 1, Oxiphos (bis-alkylpolyoxyethylene-phosphate  $[C_{mH_{2n+1}O(C_2H_4O)_m}]_2 POOH$ ,  $n = 8-10$ ,  $m = 6$ ); 2, synthanol DS-10 (monoalkylethers of polyethyleneglycol,  $C_nH_{2n+1}O(C_2H_4O)_mH$ ,  $n = 10-18$ ,  $m = 8-10$ ); 3, PKB (polymers of  $N,N$ -dialkyl- $N,N$ -diallylammonia); 4, DDS (dodecylsulphate)  $\tau_{ads} = 100$  s.

35, 36] indicate that the greatest adsorbability is observed for compounds with a triple acetylene bond, for aromatic and other unsaturated compounds and also for compounds having other weak bonds in the molecule. Introduction into a saturated organic compound of different substituents weakening the adjacent C-H bonds (alcohols, aldehydes, etc.) leads to a drastic increase in adsorbability. For phenol and other aromatic compounds, as well as for a number of synthetic surfactants (SSAS), appreciable adsorption is already observed when they are present in solution in concentrations below  $0.01 \text{ mg l}^{-1}$ , for glucose at the concentration  $1 \text{ mg l}^{-1}$  and for methanol only at  $3 \text{ mg l}^{-1}$ .

As regards the use of the concentration dependences for analytical purposes, it is important to establish the lower limit of the concentrations being measured ( $C_{min}$ ) characterizing the sensitivity of the method and the operating range determined by the linear section of the adsorption isotherm.

Taking into account the accuracy of the potentiodynamic method ( $\pm 5\%$ ), the coverage values  $\theta \geq 10\%$  are usually considered to be reliably measurable. As can be seen from Figs 5-7, such values of the parameters being measured are observed for different substances at widely different concentrations. For the most toxic organic impurities, such as oil,

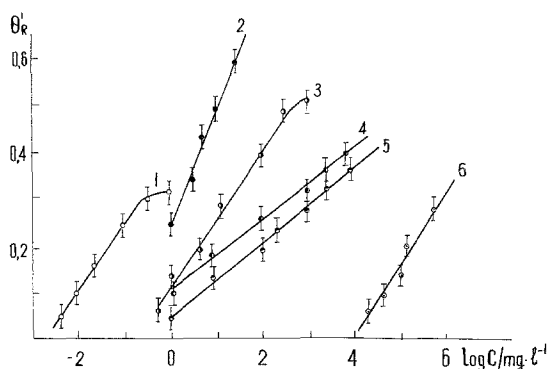


Fig. 7. Electrode coverage vs concentration of organic components of natural water in 0.5 M  $H_2SO_4$ : 1, fulvic acids; 2, albumin; 3, humic acids (supporting electrolyte 0.5 M KOH); 4, glycine; 5, glucose; 6, citric acid.  $E_{ads} = 0.4 \text{ V}$ ,  $\tau_{ads} = 100$  s.

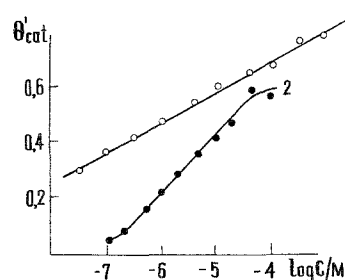


Fig. 8. Steady-state electrode coverage vs concentration of cations: 1,  $Hg^{2+}$ ; 2,  $Sn^{2+}$ ; supporting electrolyte 0.5 M  $H_2SO_4$ .  $E_{ads} = 0.2 \text{ V}$ .

benzene and phenol, the most widely used SSAS,  $C_{min} = 0.01-0.1 \text{ mg l}^{-1}$ .

The operating section of the concentration dependence includes 2-3 orders of concentration variation. It should be noted that the upper limit determined by saturation of the electrode surface can be extended by diluting the samples.

Figure 8 shows the dependences of electrode coverage on concentration in solutions of mercury and tin cations. As seen from the figure, the parameter being measured is very sensitive to concentrations of such specifically adsorbable cations. Thus, for example, for mercury  $C_{min} < 0.01 \text{ mg l}^{-1}$ , the linear section of the adsorption isotherm covering 4 orders of concentration variation. This allows the dependence to be used for analytical purposes. We examined the main features of the adsorption on a smooth platinum electrode of the cations of certain toxic metals - lead, cadmium and mercury - and showed that, with a proper choice of potential and adsorption time, they can be quantitatively determined starting from the concentration  $0.001 \text{ mg l}^{-1}$ .

In Table 1 the sensitivity of the proposed method with respect to individual substances is compared with their allowable level in water reservoirs [1] and with the minimum concentrations determinable by other methods. It is clear from the table that by means of the potentiodynamic method it is possible, for the majority of individual compounds, to determine their presence in water at the allowable level.

#### 4. Determination of the content of organic impurities (dissolved organic carbon) in waters of different composition

##### 4.1. Determination of organic impurities in fresh water

The strong dependence of the constant  $a$  (adsorbability) in Equation 1 on the organic substance nature called in question the possibility of employing the proposed electrocatalytic method for quantitative determination of dissolved organic impurities in real waters due to the presence in them of a wide variety of organic substances. For instance, surface waters usually contain carboxylic and oxycarboxylic acids: acetic, propionic, oxalic, citric, tartaric, malic acids, etc. ( $0.01-10 \text{ mg l}^{-1}$ ), humic ( $0.01-30 \text{ mg l}^{-1}$ ) and fulvic acids ( $1-100 \text{ mg l}^{-1}$ ), alcohols (up to  $2 \text{ mg l}^{-1}$ ), alde-

Table 1. Comparison of the sensitivity of the electrochemical method with other methods of determination of organic substances

Organic substance	Allowable limit ( $\text{mg l}^{-1}$ )	Detectable limit ( $\text{mg l}^{-1}$ )	
		Electrochemical method	Unified methods [3-5]
<i>Acids</i>			
formic		5.0	
maleic		0.1	
humic		0.1	0.5 spectrophotometry
fulvic		0.05	10-20 separation by 20 chemical method and COD determination
<i>Alcohols</i>			
methanol	3.0	3.0	
ethanol		1.0	
propanol	0.25	0.5	
butanol	1.0	0.2	
formaldehyde	0.05	0.3	0.05 colorimetry
<i>Aromatic substances</i>			
benzene	0.5	0.01	0.5 extraction and thin-layer chromatography 0.25 colorimetry 0.05 nitration and polarography
nitrobenzene	0.2	0.01	
phenol	0.001	0.01	0.005 colorimetry 0.005 photometry 1.0 chromatography
oil	0.5	0.3-0.5	0.1 extraction and IRS
<i>Surfactants</i>			
dodecyl sulphate	0.5	0.5	0.01 colorimetry
oxyphos	0.5	0.005	0.01 spectrophotometry
synthanol	0.5	0.01	1.0 colorimetry
PKB	0.5	0.01	1.0 extraction and IRS
glucose		1.0	10 chemical methods
glycine		0.1	
albumin		0.01	

hydes, ketones, polyfunctional carbonyl compounds ( $0.05\text{--}2.2\text{ mg l}^{-1}$ ), phenols and polyphenols, reducing sugars and polysaccharides, esters, aliphatic amines, amino acids (aspartic acid, arginine, glycine, etc.) and protein-like substances [37]. But due to too great variations in the content of individual components for a particular type of water one may consider the adsorption behavior of a sum of organic impurities as adsorption of a certain new organic compound (organic residue) with the adsorption constant  $a_1$ .

Adsorption measurements were performed in several types of real waters containing a variety of different organic substances. On the basis of experimental data obtained in preliminary investigations, the conditions were found for the reactivation of the platinum electrode in these waters in order to obtain a reproducibly clean surface (determined during the reference pulse  $I$  in Fig. 2). Alternating activation of the electrode at the potentials 1.6 and 0.0 V for 100 s before each measurement proved to be sufficient for removing from the working electrode surface organic impurities of different composition. Before the beginning of measurements or after a long interruption in the electrode operation it was subjected to this kind of activation for a longer time until a reproducibly clean surface was obtained.

In Fig. 9 are given the dependences of the platinum electrode coverage on the total concentration of dissolved organic impurities in different waters determined by the high-temperature catalytic oxidation method (HTCO). It will be seen from the figure that if, instead of individual organic substances, their mixture is present in solution, Equation 1 for the TOC content is valid as well. Thus, by determining the electrode coverage, one can assess the volume content of the sum of organic impurities in different waters.

It should be noted that, since the electrochemical method is an indirect one, in order to plot a calibration curve it is necessary for each type of water to deter-

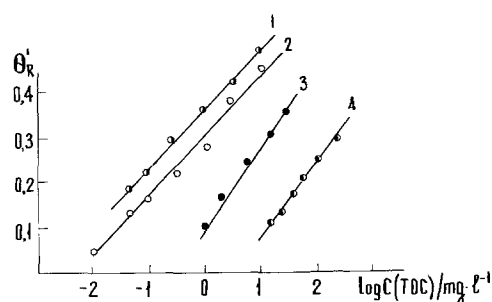


Fig. 9. Electrode coverage vs total organic carbon content in different types of water: 1, 2, ground water; 3, river water; 4, sewage water.

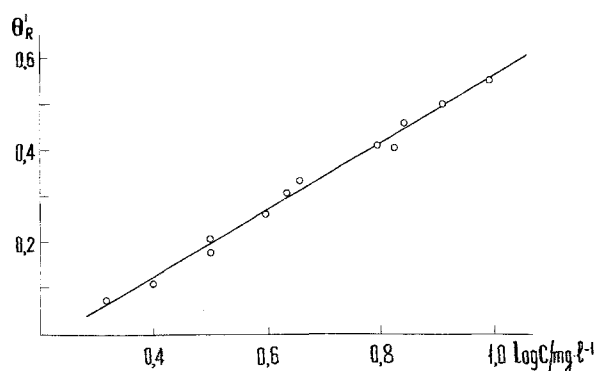


Fig. 10. Calibration curve for determination of concentration of organic impurities in water of Moscow River-Oka Basin.

mine the concentration of organic impurities even for a single point by a direct method or to use a standard solution of known concentration simulating the composition of a particular water.

In plotting the calibration curves of the type shown in Fig. 9 steady-state coverage values were not always used. For analytical purposes the adsorption time was chosen such that it should be sufficient for obtaining medium coverage values (0.1–0.6), i.e. under the conditions where it could be measured with sufficient accuracy. Thus in Fig. 10 a calibration curve of this kind is given for waters of the Moscow River-Oka Basin with an adsorption time of 2 min.

The presence of a linear logarithmic dependence of the parameter being measured on concentration has its advantages and disadvantages. On the one hand, it covers a large concentration range from  $10^{-2}$  to  $10 \text{ mg l}^{-1}$ , but on the other hand, the accuracy of determination of the concentration in the case of a logarithmic dependence is not high. To increase the sensitivity in a narrow concentration range one can use kinetic dependences. In Fig. 11 the dependences of electrode coverage on adsorption time measured in river water with different content of organic impurities are presented. Using these data one can calculate the adsorption rate at the initial moment (at  $\theta = 0$ ). Experiments show that the adsorption rate is proportional to the volume concentration of organic

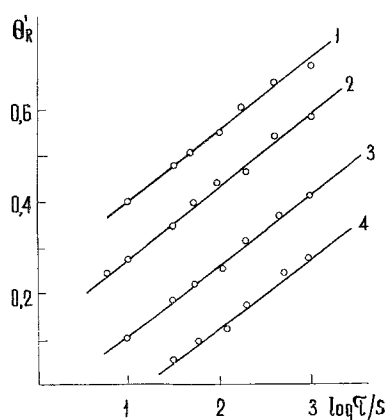


Fig. 11. Dependence of electrode coverage with sum of organic substances present in river water on adsorption time in  $0.5 \text{ M H}_2\text{SO}_4$  at TOC concentration in  $\text{mg l}^{-1}$ : 1, 10; 2, 6.2; 3, 3.8; 4, 2.6.  $E_{\text{ads}} = 0.4 \text{ V}$ .

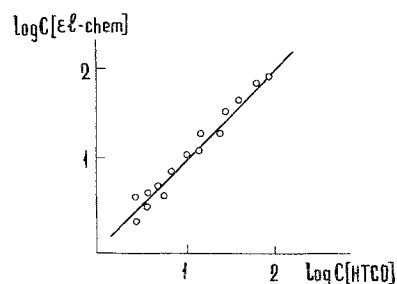


Fig. 12. Relation between organic substance concentrations in standard solutions determined by electrochemical method ( $C_{\text{el-chem}}$ ) and by HTCO method ( $C_{\text{HTCO}}$ ).

substances, so that it is possible to determine the time in which a certain constant coverage value is reached, this time being lower the higher the volume concentration.

To check the electrochemical method the results obtained in determination of the concentration of organic impurities in standard solutions were compared with the data of the analysis by the high-temperature catalytic oxidation method (Fig. 12). As is evident from the figure, there is good agreement between the data obtained by the two methods.

Table 2, which lists the results of the determination of the impurities in the natural waters of the Moscow River and Oka Basins, also show good agreement between the measurements by the electrochemical and the high-temperature catalytic oxidation methods.

The results of measurements of the platinum elec-

Table 2. Determination of the content of organic impurities in natural waters of the basins of Moscow and Oka Rivers by electrochemical method and by high-temperature catalytic oxidation method (HTCO)

Sample N <sup>a</sup>	$C_{\text{org}} (\text{mg l}^{-1})$	
	by HTCO method	by electrochemical method
1	3.3	3.0
2	9.9	9.9
3	6.6	6.2
4	6.3	6.9
5	4.6	4.3
6	3.4	3.5
7	3.4	3.6
8	6.2	6.1
9	2.6	2.8
10	2.6	2.7
11	6.7	6.9
12	3.9	4.0
13	4.3	4.8
14	7.5	7.3
15	2.6	2.9
16	7.0	6.7
17	2.9	2.7
18	3.9	4.3
19	3.2	3.2
20	3.2	3.2
21	4.3	4.2
22	4.3	4.2
23	5.9	5.5
24	2.6	2.6
25	3.2	3.2

<sup>a</sup> Different samples correspond to different places in the rivers.

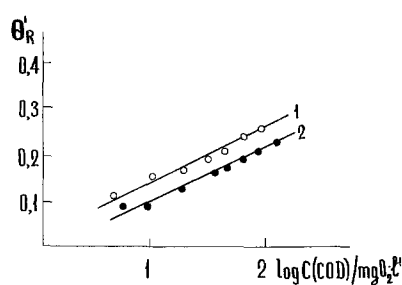


Fig. 13. Electrode coverage vs concentration in COD units in different sewage waters.

trode coverage in effluents were compared with those of COD determinations in each sample examined (Fig. 13). It was found that the parameter being measured depends linearly on the logarithm of COD.

Comparison of the electrochemical method with other methods demonstrates its applicability as an analytical method to determination of total dissolved organic carbon in real water.

It should be noted that the proposed method has a high sensitivity. As is clear from Fig. 9 (Curves 1 and 2), with its use it is possible to determine organic impurities at the level of 0.01–0.1 mg l<sup>-1</sup> in ground waters, where other methods (e.g. COD determination) are inapplicable.

#### 4.2. Differentiation of organic impurities contained in water

A disadvantage of the electrochemical method is its lack of specificity. In this respect it does not differ from any other method of TOC determination.

For differentiation of the organic substances being determined two oxidative potential steps were introduced into the program of an automatic analyser (Fig. 2, V and VII) by means of which adsorbed mixtures are separated into easy-, medium- and difficult-to-oxidize categories. Separation is carried out as follows. After the adsorption of different organic particles the potential 0.94 V is applied to the electrode for 5 s. During this period all readily oxidizable particles undergo oxidation and the surface becomes partly free. The sum of the medium- and difficult-to-oxidize impurities remaining on the surface is determined by a potentiodynamic pulse VI similar to the pulses II and IV. Then the adsorbed substances are subjected to oxidation at a more positive potential, 1.33 V, whereupon only the difficult-to-oxidize impurities, which are determined by the measuring pulse VIII, remain on the surface. All these operations are performed by the automatic device and the charge values determined in operations VI and VIII are compared with the reference charge II corresponding to a free electrode surface. Thus when the whole cycle of programmed operations has been performed, three sets of figures appear on the analyser display: the electrode coverage corresponding to the total sum of organic substances present in solution, those corresponding to the amount of medium-oxidizable impurities and those corresponding to

the amount of difficult-to-oxidize ones. This differentiation, as applied to analysis of real natural waters, is in most cases qualitative, i.e. individual substances are not singled out. Separate quantitative determination of individual substances is possible only in certain specific situations, for example, in the case of analysis of effluents from a plant producing phenol-formaldehyde resins. The effluents contain mainly two components: phenol and formaldehyde, radically different in oxidizability. In these effluents the concentration of the most strongly adsorbable component, phenol, varied from  $5 \times 10^{-6}$  to  $7 \times 10^{-5}$  M, the concentration of formaldehyde from  $10^{-4}$  to  $10^{-2}$  M. As was determined by special experiments, in these proportions both substances are adsorbed additively in accordance with their content in solution. Table 3 lists the results of the analysis by the proposed method of model phenol and formaldehyde solutions. It is evident that individual determination of phenol and formaldehyde in their mixture yielded good results.

#### 4.3. Determination of organic impurities in sea water

Of great practical importance is the determination of organic impurities in sea water and mineralized ground waters containing chlorides in high concentration. In this case it is impossible to use acid supporting electrolytes as, in acid solutions, chloride ions are known to compete with organic substances for adsorption sites on platinum surfaces [38, 39]. In alkaline solutions, however, chloride ions are practically not adsorbed on platinum over a wide potential range. Since addition of alkaline solution (1 M NaOH) to mineralized waters brings about precipitation of the hydroxides of metals contained in them (e.g. magnesium and calcium) we chose as the supporting electrolyte 0.2 M phosphate buffer solution with pH = 8, which is close to the pH value in natural sea water.

Measurements showed that addition of chloride ions up to the concentration 10–20 g l<sup>-1</sup>, corresponding to their content in sea water, does not decrease hydrogen adsorption in a phosphate buffer solution (pH = 8) ( $\theta' < 0.05$ ) but alters the proportion of strongly and weakly bound hydrogen forms [20].

Figure 14 shows the dependences of electrode coverage on the concentration of individual organic

Table 3. Determination of phenol and formaldehyde in a mixture (model solutions)

$C_6H_5OH$ (M)		$CH_2O$ (M)	
Introduced	Found	Introduced	Found
$6.3 \times 10^{-6}$	$7.15 \times 10^{-6}$	$2.0 \times 10^{-4}$	$2.8 \times 10^{-4}$
$5.0 \times 10^{-6}$	$5.85 \times 10^{-6}$	$5.0 \times 10^{-4}$	$5.4 \times 10^{-4}$
$1.0 \times 10^{-5}$	$1.3 \times 10^{-5}$	$1.2 \times 10^{-3}$	$1.1 \times 10^{-3}$
$3.2 \times 10^{-5}$	$2.9 \times 10^{-5}$	$3.0 \times 10^{-3}$	$2.8 \times 10^{-3}$
$5.0 \times 10^{-5}$	$6.0 \times 10^{-5}$	$5.0 \times 10^{-3}$	$4.5 \times 10^{-3}$
$7.0 \times 10^{-5}$	$7.8 \times 10^{-5}$	$9.2 \times 10^{-3}$	$7.9 \times 10^{-3}$



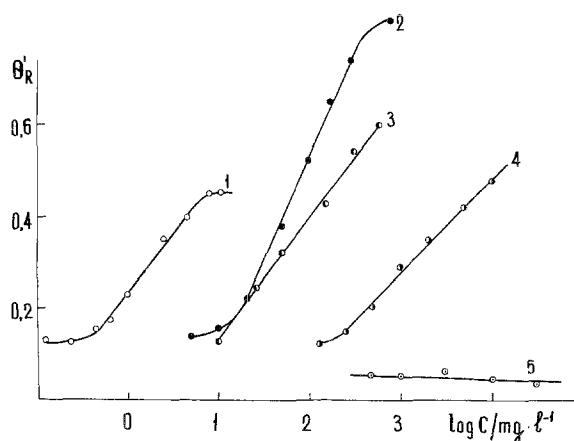


Fig. 14. Electrode coverage vs concentration of organic substances (supporting electrolyte 0.2M phosphate buffer solution (pH = 8) + 0.2M NaCl).  $E_{ads} = 0.4$  V,  $\tau_{ads} = 300$  s. 1, Benzene; 2, formaldehyde; 3, ethanol; 4, methanol; 5, NaCl with 0.2M phosphate buffer solution as supporting electrolyte).

substances in a buffer solution with addition of a high concentration of chloride ( $10 \text{ g l}^{-1}$  NaCl).

A linear dependence  $\theta'/\log C$  is also observed in the presence of phosphates and chlorides, but the linear section narrows down due to decrease in sensitivity in the low concentration range due to the influence of phosphate ion coadsorption, and in some cases due to decrease of maximum coverage. Thus, for example for benzene, the operating range of determinable concentrations is observed from  $0.5$  to  $5 \text{ mg l}^{-1}$  in distinction to  $0.01$ – $10 \text{ mg l}^{-1}$  in acid solutions.

One of the most frequently determined impurities in sea water is oil. For this reason adsorption measurements in phosphate buffer solutions and in real sea water were performed in the presence of mixtures of oil and benzene as model substances. The oil solutions were prepared by saturation of the supporting electrolyte or sea water under the oil or benzene layer for 24 h with stirring at regular intervals. Then the water fraction saturated with organic substance was separated by means of a separatory tunnel. The amount of organic substance was determined by the international arbitrary extraction method [40]. In this method the organic substances from aqueous solutions are extracted with  $\text{CCl}_4$  and determined quantitatively by IR spectroscopy from the intensity of the adsorption band of the C–H groups in the benzene ring at  $2920 \text{ cm}^{-1}$ .

In Fig. 15 the results of these experiments for an adsorption time 100 s are shown. The dependences when plotted as  $\theta'/\log C$  show a well-defined linear section. The minimum determinable oil concentration ( $C_{min}$ ) in sea water is  $0.3$ – $0.5 \text{ mg l}^{-1}$ , which is at the allowable level.

It should be pointed out, in comparing the adsorption electrochemical method with the arbitrary extraction method, that the latter has a somewhat higher sensitivity ( $0.05$ – $0.1 \text{ mg l}^{-1}$ ), but for analysis by the extraction method of waters containing a minimum amount of organic substance a 2–3 l sample is to be handled, which increases the analysis time to several hours. In our method the sample volume is

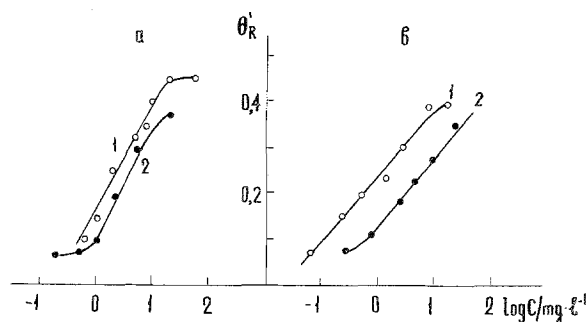


Fig. 15. Calibration curves for determination of impurities. (a) Benzene, (b) oil in different supporting electrolyte solutions: 1, 0.2M phosphate buffer (pH = 8) + 0.2M NaCl; 2, sea water (pH = 8).  $E_{ads} = 0.4$  V,  $\tau_{ads} = 100$  s.

10–15 ml, the analysis time is 3–15 min, and the accuracy is 10–15%. Thus we see that the electrochemical adsorption method can be used as a rapid and sufficiently accurate method of analysis of organic impurities in sea water and mineralized ground waters.

## 5. Conclusions

A new electrochemical method for determination of total organic carbon and metal cations in real waters is proposed which has the following advantages: high sensitivity; rapidity of analysis; automatic performance of analyses; low cost and small overall size of the equipment used; possible use of self-contained power sources; and no need for previous separation of inorganic carbon compounds.

On the basis of this method a number of analysers have been devised. For instance, 'analyser of the water quality, digital, potentiodynamic' (AQWEL) incorporating a microcalculator 'Elektronika B3-34' can be used for control of natural waters — river, lake and sea water, industrial effluents and sewage water, and extra pure water for the electronics industries. The weight of the device is 1.5 kg, and its overall dimensions are  $14 \times 28 \times 19$  cm. For determination of dissolved organic carbon the range of the analyser is  $0.1$ – $1000 \text{ mg l}^{-1}$ , the sensitivity of the method is  $0.01 \text{ mg l}^{-1}$ , the time of analysis 3–15 min and the accuracy is 10%. The analyser differentiates organic impurities according to their oxidizability into easy-, medium- and difficult-to-oxidize categories. In the determination of heavy metals the sensitivity of the method is  $0.001 \text{ mg l}^{-1}$ . Toxic metal (mercury, lead, cadmium) mixtures are determined separately.

The application of this analyser demonstrates the wide potentialities of electrocatalytic adsorption methods of determination of organic impurities and heavy metals in natural, drinking and sewage waters.

## References

- [1] 'Predelno-dopustimye koncentratsii vrednykh veshchestv v vozdukh i vode', Chimiya, Moskva (1975) (in Russian).
- [2] 'Vrednye veshchestva v promyshlennosti' (edited by E. N. Levina and I. D. Gadaskina), Chimiya, Leningrad (1985) (in Russian).

- [3] 'Unifitsirovannye metody analiza vody' (edited by Yu. Yu. Lurie), *Chimiya*, Moskva (1971) p. 74 (in Russian).
- [4] 'Unifitsirovannye metody issledovaniya kachestva vod, Part 1, Metody chimicheskogo analiza vod', SEV, Moskva (1977) p. 431.
- [5] W. Leite, 'Die Analyse der organischen Verunreinigungen in Trink Brauch und Abwässern', Wissenschaftliche Verlagsgesellschaft MBH, Stuttgart (1972).
- [6] N. Watanabe, T. Kavasome and T. Kudo, *J. Environ. Pollut. Control* **12** (1976) 789.
- [7] C. E. Van Holl and V. A. Stenger, *Water Sewage Works* **111** (1964) 266.
- [8] P. Wölfel, W. Schuster and H. Sontheimer, *J. Wasser-Abwasser Forsch. B* **8** (1975) 143.
- [9] S. V. Lutsarev and A. V. Smetankin, in 'Metody issledovaniya organicheskogo veshchestva v okeane' (edited by E. A. Romankevich), Nauka, Moskva (1980) p. 32 (in Russian).
- [10] R. S. Nicholson, *Analyt. Chem.* **44** (1972) 478R.
- [11] E. Barendrecht, in 'Electroanalytical Chemistry' (edited by A. J. Bard), Edward Arnold, London (1967) Vol. 2.
- [12] R. Neeb, 'Inverse Polarographie und Voltammetrie', Verlag Chemie, Weinheim Bergstr. (1969).
- [13] Kh. Z. Brainina, *Talanta* **18** (1971) 513.
- [14] Kh. Z. Brainina and E. Ya. Neiman, 'Tverdofaznye reaktzii v elektroanaliticheskoi khimii', *Chimiya*, Moskva (1982) (in Russian).
- [15] M. W. Breiter and S. Gilman, *J. Electrochem. Soc.* **109** (1962) 622, 1099.
- [16] S. Gilman, *J. Phys. Chem.* **66** (1962) 2657; **67** (1963) 78, 1898.
- [17] V. S. Bagotzky and Yu. B. Vassilyev, *Electrochim. Acta* **11** (1966) 1439; **12** (1967) 1323; **16** (1971) 2141.
- [18] Yu. B. Vassilyev, V. S. Bagotzky, O. A. Khazova, V. V. Cherny and A. M. Meretsky, *J. Electroanal. Chem.* **98** (1979) 253, 273.
- [19] Yu. B. Vassilyev, V. S. Bagotzky, O. A. Khazova, N. N. Krasnova and T. A. Sergeeva, *Electrochim. Acta* **26** (1981) 545.
- [20] V. S. Bagotzky, Yu. B. Vassilyev, J. Weber and J. N. Pirtskhalava, *J. Electroanal. Chem.* **27** (1970) 31.
- [21] M. Watanabe and S. Motoo, *J. Electroanal. Chem.* **72** (1975) 259, 267, 275; **69** (1976) 429.
- [22] N. Furuya and S. Motoo, *J. Electroanal. Chem.* **72** (1976) 165; **78** (1977) 243; **88** (1978) 151; **98** (1979) 195; **100** (1979) 771.
- [23] Yu. B. Vassilyev, V. S. Bagotzky, N. V. Osetrova and A. A. Mikhailova, *J. Electroanal. Chem.* **97** (1979) 63.
- [24] M. S. Chemeris, A. G. Stromberg, N. A. Kolpakova and Yu. B. Vassilyev, *Elektrokhimiya* **11** (1975) 1060; **12** (1976) 52 (in Russian).
- [25] L. Formaro and S. Trasatti, *Analyt. Chem.* **40** (1968) 1060.
- [26] B. B. Damaskin, O. A. Petrii and V. V. Batrakov, 'Adsorbtsiya organicheskikh soedineniy na elektrodakh', Nauka, Moskva (1968) (in Russian).
- [27] M. W. Breiter, 'Electrochemical Processes in Fuel Cells', Springer Verlag, Berlin (1969).
- [28] Yu. B. Vassilyev and V. S. Bagotzky, in 'Problemy kinetiki i kataliza', Vol. 16 (edited by O. V. Krylova and M. D. Shibanova), Nauka, Moskva (1975) p. 260 (in Russian).
- [29] Patent USSR No. 1157940, Bul. Izobretenij No. 2 (1986) p. 285 (in Russian).
- [30] J. E. Oxley, G. K. Johnson and B. T. Buzalski, *Electrochim. Acta* **9** (1964) 897.
- [31] Yu. I. Podlovtsenko and E. P. Gorgonova, *Dokl. AN SSSR* **156** (1964) 673 (in Russian).
- [32] D. M. Dražić and V. Dražić, *Electrochim. Acta* **11** (1966) 1235.
- [33] S. F. Chernyshov, *J. Res. Inst. Catalysis Hokk. Univ.* **30** (1982) 179.
- [34] Patent USSR No. 1157441, Bul. Izobretenij No. 19 (1985) p. 165. Patent USSR No. 1158913, Bul. Izobretenij No. 20 (1985) p. 173 (in Russian).
- [35] O. A. Petrii and A. G. Pshenichnikov, in 'Problemy elektrokataliza' (edited by V. S. Bagotzky), Nauka, Moskva (1982) p. 41 (in Russian).
- [36] V. E. Kazarinov, G. Horanyi, Yu. B. Vassilyev and V. N. Andreev, in 'Itogi nauki i tekhniki. Elektrokimiya' (edited by Yu. M. Polukarov), VINITI, Moskva (1985) Vol. 22 (in Russian).
- [37] G. M. Varshal, I. Ya. Koshcheeva, I. S. Sirotkina, T. K. Valiukhanova, L. I. Intskirveli and N. S. Zamokina, *Geokhimiya* **4** (1979) 598 (in Russian).
- [38] G. N. Pirtskhalava, Yu. B. Vassilyev and V. S. Bagotzky, *Elektrokhimiya* **6** (1970) 1144 (in Russian).
- [39] V. A. Gromyko, T. B. Tsygankova, V. B. Gaidadymov, Yu. B. Vassilyev and V. S. Bagotzky, *Elektrokhimiya* **9** (1973) 1685 (in Russian).
- [40] S. G. Oradovsky, in 'Metody issledovaniya organicheskogo veshchestva v okeane' (edited by E. A. Romankevich), Nauka, Moskva (1980) p. 249 (in Russian).