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## STUDY OF PROCESSES DURING ELECTROLYSIS OF ORGANIC DYE SOLUTION BY MEANS OF ION-PHOTON SPECTROMETRY

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Spectral composition and quantum yield of radiation of the excited particles sputtered by an ion beam from surfaces of the dried sediment formed on electrodes at the electrolysis of the organic dye were studied by the method of ion-photon spectrometry. A correspondence between processes taking place near the electrode during the electrolysis of the organic dye solution and the composition of excited particles knocked out from the dried sediment formed on the electrodes was shown.

**KEY WORDS:** ion-photon spectrometry, excited particles, spectral composition, quantum yield of radiation, organic dyes, electrolysis

### ДОСЛІДЖЕННЯ ПРОЦЕСІВ, ЩО ПРОТІКАЮТЬ ПРИ ЕЛЕКТРОЛІЗІ РОЗЧИНУ ОРГАНІЧНОГО БАРВНИКА, МЕТОДОМ ІОННО-ФОТОННОЇ СПЕКТРОМЕТРІЇ

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Методом іонно-фотонної спектрометрії досліджено спектральний склад та квантовий вихід випромінювання збуджених частинок, вибитих іонним пучком з поверхні висушених осадів, що утворилися на електродах при електролізі органічного барвника. Показано наявність кореляції між процесами, що протікають поблизу електродів у процесі електролізу органічного барвника та складом збуджених частинок, вибитих з поверхні висушених осадів, що утворилися на електродах

**КЛЮЧОВІ СЛОВА:** іонно-фотонна емісія, збуджені частинки, спектральний склад, квантовий вихід випромінювання, органічні барвники, електроліз

### ИССЛЕДОВАНИЕ ПРОЦЕССОВ, ПРОТЕКАЮЩИХ ПРИ ЭЛЕКТРОЛИЗЕ РАСТВОРА ОРГАНИЧЕСКОГО КРАСИТЕЛЯ, МЕТОДОМ ИОННО-ФОТОННОЙ СПЕКТРОМЕТРИИ

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Методом ионно-фотонной спектрометрии исследован спектральный состав и квантовый выход излучения возбужденных частиц, выбитых ионным пучком с поверхности высушенных осадков, образовавшихся на электродах при электролизе органического красителя. Показано наличие корреляции между процессами, протекающими вблизи электродов в процессе электролиза органического красителя и составом возбужденных частиц, выбитых с поверхности высушенных осадков, образовавшихся на электродах.

**КЛЮЧЕВЫЕ СЛОВА:** ионно-фотонная эмиссия, возбужденные частицы, спектральный состав, квантовый выход излучения, органические красители, электролиз

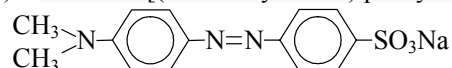
Solutions of substances belonging to azo dyes are widely used for diagnostics and treatment of various diseases [1, 2]. The study of the processes taking place during their dissolution is an important task. Methods based on the phenomena of secondary particles emission under ion bombardment of solids such as secondary ion mass-spectrometry (SIMS) and ion-photon spectrometry (IPS) are widely used. One of them (ISP) based on the phenomenon of ion-photon emission (IPE) which consists in knocking out of the particles in the excited states from the surface followed by emissions of photons. In our earlier papers [3, 4] the possibility of using ion-photon spectroscopy (IPS) for studies of organic compounds: dyes, lipids, and their mixtures, was considered. Original substances as well as sediments obtained by recrystallization of their water and alcohol solutions were studied. It was found that the number of excited particles ejected from the samples by ion bombarded is changing when going from the initial sample to the recrystallized precipitation. Moreover, the yield of excited particles depends both on the properties of the dye (its structure and solubility in various solvents) and on the method of sample preparation (range of recrystallization temperature, solvent properties). These results clearly show that there is a correspondence between the method of the sample preparation and

the yield of excited particles under ion bombardment. Thus analyzing IPE parameters of recrystallized substances the information about the processes occurring during their dissolution can be obtained.

Purpose of this work were analyzed by means of IPS of samples of substance precipitations obtained on a surface of the electrode when flowing the electrical current through the dye water solution. Comparison of obtained data with the known information about the processes in electrolytes allows us to estimate the applicability of IPS for studying the processes in organic compound solutions via analysis of their precipitations.

### EXPERIMENT

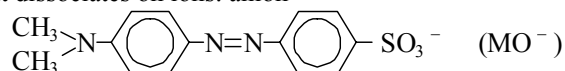
In this work methyl orange dye (MO) – sodium 4-[(4-dimethylamino) phenyldiazenyl] benzenesulfonate



was studied [5] as it widely used for the analysis of processes in complex organic systems. Samples were prepared in a specially build electrolytic bath. Saturated MO water solution of red-orange colour was used as an electrolyte. Graphite plates of  $1 \times 16 \times 1 \text{ mm}^3$  size were used as electrodes. DC voltage of 8 V was applied to the electrodes. An electrolysis procedure was performed at room temperature and lasted 60 min.

During electrolysis gaseous products were segregated on the cathode. Foaming of the electrolyte was observed on the anode which presumes forming of gas bubbles and fine-dispersed precipitation. The electrolyte changed its colour from red-orange to crimson one. The graphite anode was breaking down during all electrolysis procedure. Graphite particles felt into solution bulk and formed a suspension. The electrolyte got dark-red colour and lost its transparency towards to the end of the experiment.

During dissolution of the dye it dissociates on ions: anion



and cation  $\text{Na}^+$ . Oppositely charged dye ions drifting under the influence of the electrical field to the different electrodes cause oxidation-reduction reactions on the electrodes resulted in their changing. Material of the cathode (sample CS), of the anode (sample AS) and the sediment from the near-electrode area (sample AD 1) were studied by means of IPS. The suspension that was formed in the solution bulk during the electrolysis was dried and studied in a similar way (AD 2). As the reference sample (RS) the sediment prepared by recrystallization from the saturated water MO solution at the room temperature was used.

IPE parameters were carried out for all samples on the experimental installation described in [6]. The ion source (IS) generated mass-separated 20 keV argon ion beam of  $10 \div 20 \mu\text{A} \cdot \text{cm}^{-2}$  current density. The target was positioned in the chamber (TC) so that the incidence angle of the ion beam was  $45^\circ$  to the target surface normal. The pressure in the TC was  $(1 \div 2) \cdot 10^{-4} \text{ Pa}$  and did not change when operating the IS. Radiation of excited particles sputtered from the target surface by an ion beam was fed out through TC window and focused by achromatic lens on the entrance slit of the setup for collection and analysis of radiation. The geometry of radiation collection permitted determination of a full amount of photons emitted by excited particles leaving the surface. Emission spectra in the wavelengths range  $250.0 \div 800.0 \text{ nm}$  were recorded by photoelectric registration system, operating in photon counting mode.

### RESULTS AND DISCUSSION

Optical emission spectra of excited particles sputtered from the sample surface during ion bombardment were obtained. The fragments of these spectra are shown in Fig. 1. The spectral composition these spectra were determined. Quantum yield for lines with intensity of not less than two times exceeding the background level were calculated.

The analysis of spectra of exited particles sputtered from all samples has shown that following lines were present in all spectra:

- emission lines of hydrogen atom ( $\lambda$  486.1 nm,  $\text{H}_\beta$ ;  $\lambda$  56.2 nm,  $\text{H}_\alpha$ );
- molecular bands of CH radical ( $\lambda$  431.2 nm, system 430 nm, transition  $^2\Sigma - ^2\Pi$ , g.s.;  $\lambda$  387.2 nm, system 390 nm, transition  $^2\Sigma - ^2\Pi$ , g.s.);
- lines of Na I spectrum ( $\lambda$  568.2, 568.8, 588.9, 589.6, 330.2 nm);
- number cants of a molecule band that is not yet interpreted.

It should be noted that in emission spectra of particles knocked out from the samples RS, CS, AD 1 and AD 2, emission lines of aluminium, magnesium and calcium atoms were observed. These atoms were probably present in the dye as the impurity substance since these lines were also registered in the IPE spectra of the solid target make up from pressed powder of the corresponding dye. In the spectra of deposition formed on the positive electrode (AS) lines related to the impurity not observed.

Quantum yield of emission ( $\gamma_\lambda$ ) – the number of photons of the analysed wavelength per one incident ion – was calculated (see the Table 1) for the main emissions (lines of hydrogen atom and molecular band of CH radical) and the most intensive characteristic emissions (lines of Na atom). According to [6] spectral line intensity  $I_\lambda$  is related to the quantum yield as  $I_\lambda \sim \gamma_\lambda \cdot (hc / \lambda)$ , where  $hc / \lambda$  – quantum energy. Values of  $\gamma_\lambda$  for all lines of impurities which present at spectra of different samples are shown in the Table 2.

Table 1

Quantum yields of main and characteristic emissions

$\lambda$ , nm	Interpretation	$\gamma_\lambda$ , $10^{-6}$ phot./ion				
		The water solution of methyl orange dye				
		RS (a)	CS (b)	AS (c)	AD 1 (d)	AD 2 (e)
431.2	CH	2	5.5	1.4	1.9	3.2
486.1	H $\beta$	0.5	1.4	0.3	0.4	0.7
656.2	H $\alpha$	6.6	17.3	4.2	3.9	9
568.2; 568.8	Na I	3.1	0.9	-	1.3	2.1
588.9; 589.6	Na I	250.4	24.8	0.5	95.6	204.2
330.2	NaI	2.2	0.5	-	0.8	0.8

Table 2

Quantum yields of impurity lines in different samples spectra

$\lambda$ , nm	Interpretation	$\gamma_\lambda$ , $10^{-6}$ phot./ion			
		RS (a)	CS (b)	AD 1 (c)	AD 2 (d)
365.1	Al II	0.2			0.2
365.5	Al II	0.2			0
382.9; 383.2	Mg I	0.3			0.3
383.8	Mg I	0.4			0.4
393.3	Ca I	1.3		0.1	1.3
394.4	Al I	0.6	*		0.4
396.1	Al I	0.9	*		0.5
396.8	Ca I	0.9		0.2	0.4
422.7	Ca I	3.3		0.3	2.7
442.5	Ca I	0.4			0.5
445.4	Ca I	0.5			0.6
517.2; 518.3	Mg I	1			0.8
526.5; 5270	Ca I	0.6			0.6
534.9	Ca I	0.6			0.5
559.0; 559.8	Ca I	3.1			2.5
305.0	Al I	0.7			
305.7	Al I	1.2			
306.4	Al I	1.4			1.1
308.2	Al I	4.4	1.2	0.9	3.5
309.2	Al I	5.2	2.1	1.6	2.7
643.9	Ca I	4.3			3.3
646.2	Ca I	3.1			2.4
649.3	Ca I	1.7			1.3

\*The lines were blending by the band of 390 nm (0,0) system,  $^2\Sigma - ^2\Pi$ , transition of g.s. CH molecule

Let's consider each spectrum shown in Fig.1. In Fig.1a the emission spectrum of excited particles sputtered from RS is shown. Lines of hydrogen, sodium, aluminum, magnesium, calcium atoms and the band of CH radical are present at the spectrum. Wavelengths of the most intensive lines are marked in Fig. 1a. Wavelengths for impurities are given in the Table 2. Following the data in the Table 1(column a) one can conclude that intensities of characteristic lines of emissions of the sample RS are highest.

In Fig.1b emission spectrum of excited particles sputtered from CS is shown. Lines of hydrogen, sodium, aluminum excited atoms, and very intensive bands of the CH molecule ( $\lambda\lambda$  431.2 nm, 387.2 nm) are present at the spectrum. According to the data of the Table 1 (column b) lines of hydrogen atoms in the spectrum of excited particles sputtered from CS are the most intensive in comparison to other samples spectra. In comparison to RS spectrum,  $\gamma_\lambda$  surplus is 2.8 times for  $\lambda$  656.2 nm line and 2.6 times for  $\lambda$  656.2 nm line. The  $\gamma_\lambda$  value for CH ( $\lambda$  431.2 nm) band is 2.7 times higher. The intensity of sodium resonant line is by the order of magnitude less than in the RS spectrum. Intensities of aluminum lines which present in the spectra are lower than those for RS.

In the AS spectrum weak lines of hydrogen atoms and the band ( $\lambda$  431.2 nm) of CH radical (see Fig. 1c) are present. The weak resonant sodium line is also there but its quantum yield is 500 times lower than in RS spectrum (Table 1, column c).

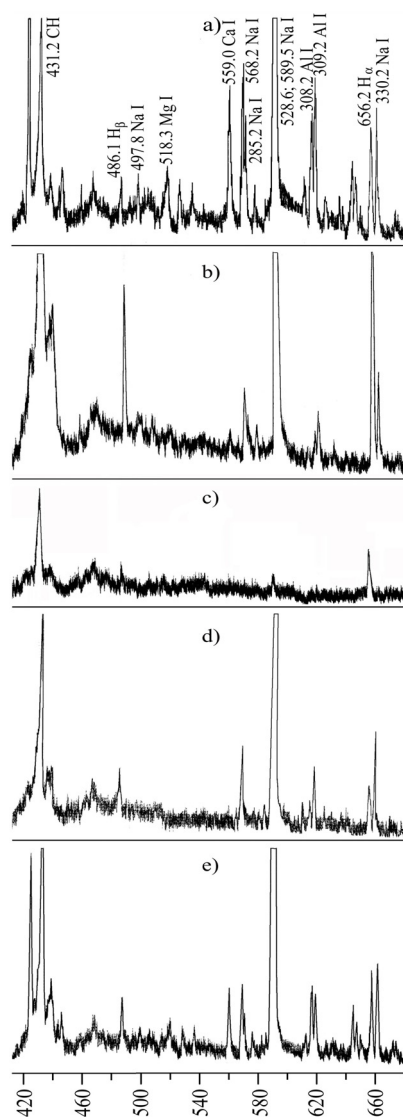


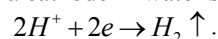
Fig. 1. Emission spectra of excited particles sputtered from different samples

- a) the sediment got by the recrystallization from the saturated water MO solution (RS);  
 b) cathode material (CS);  
 c) anode material (AS);  
 d) the sediment from near-electrode area (AD 1);  
 e) the dried electrolyte sediment (AD 2).

Lines of hydrogen, sodium, aluminum and calcium excited atoms, and the band of the CH radical ( $\lambda$  431.2 nm) are present at AD 1 spectrum (Fig. 1d). According to the Table 1, column d, the intensity of  $H_{\alpha}$  line of this sample is the weakest in comparison to other samples, even though intensities of  $H_{\beta}$  and CH lines are similar to those in RS spectrum. The intensity of resonant sodium line is 2.5 times lower than in RS spectrum.

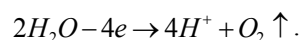
In AD 2 spectrum (Fig. 1e) lines of hydrogen, sodium, aluminum, magnesium and calcium excited atoms and the band of the CH radical ( $\lambda$  431.2 nm) are observed. Intensities of hydrogen atom lines are higher in this spectrum than in RS and AD 1 spectra. Intensities of aluminum and calcium lines are higher than in AD 1 spectrum. The intensity of resonant sodium line is 2 times higher than in AD 1 spectrum and 1.4 times lower than in RS spectrum. AD 2 spectrum is similar to RS spectrum with the only difference of observed lines.

We analyzed the obtained data basing on the theory of electrolytic dissociation. According to [7] positive ions should be restored on the cathode during electrolysis. In our case these are ions of hydrogen, sodium and impurity metals. As known [7], standard electrode potentials of K, Ca, Na are:  $E_{K/K^+}^0 = -2.959 V$ ,  $E_{Ca/Ca^{2+}}^0 = -2.866 V$ ,  $E_{Na/Na^+}^0 = -2.714 V$ ,  $E_{Al/Al^{3+}}^0 = -1.662 V$ . Really the hydrogen is restored on a cathode in water solution:

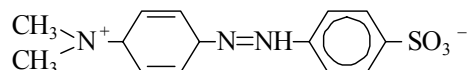


Indeed according to Fig. 1b and the data of the Table 1, column b hydrogen lines in CS sample spectrum are the most intensive compared to other samples. Concerning presence of sodium and aluminum weak lines in the spectrum, ions of these metals move under the influence of electrical field into close to the cathode area. When the cathode was removed from the electrolyte solution a part of these ions were absorbed by the cathode (material). The absence of magnesium lines in the spectrum is a result of its trace in the solution. The highest intensity of CH band in the spectrum of CS sample in comparison to others suggests that hydrogen cations interacted with graphite electrode forming CH radicals.

During electrolyze of anions  $OH^-$  and anion  $MO^-$  are oxidized on the anode. Oxidizing of  $OH^-$  hydroxyl group resulted in oxygen release:



In this connection an excess of positive hydrogen ions in near-anode area was formed. The MO dye is a salt of a weak acid [8]. Reacting with hydrogen cations it turned into protonated (acidic) form:



of red color [9]. The additional evidence of creating protonated MO form near the electrode could be the color of the near-anode suspension. As known [10], MO dye is an acid-base indicator and changes its color with change of the medium acidity. Crimson color of the near-anode suspension indicated high acidity of the medium. Hydrogen atoms and radical CH emissions which were observed in AS sample spectra were knocked out from the dye molecule. The presence of weak resonant line of Na in the spectrum is probably an experiment feature. The electrodes were for some time in the electrolyte without applying electrical field. During this time absorption of sodium ions by the anode material is possible.

As to the AD 1 и AD 2 samples, their spectra are similar to the RS sample spectra. They do not give any information on processes taking place in the solution during electrolysis. Rather high intensities of hydrogen lines in the spectra of the electrolyte sediment are due to the presence of graphite anode particles in the sediment as the result of anode destruction during electrolysis.

### CONCLUSIONS

Samples of cathode and anode materials used for electrolysis of the organic water solution of dye MO were studied.

Qualitative and quantitative comparison of emission spectra of excited particles and the sediment obtained by recrystallization from the water solution of a dye were carried out by means of IPS.

It was shown that the emission spectra of excited particles sputtered from a surface of high named samples have considerable differences.

The correspondence between the type of excited particles sputtered from the electrode surface and redox processes on electrodes during the electrolysis was shown.

The obtained data allows conclude that IPS method could be used for studying processes in organic dye solutions via the analysis of their sediments.

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