

# Investigation of organic systems by ion-photon spectroscopy

I.A. Afanas'eva, V.V. Bobkov, V.V. Gritsyna, D.I. Shevchenko

**Abstract.** We study spectral composition, quantum yield and spatial intensity distribution of radiation of excited particles, escaping from the surface of some organic dyes and their mixtures with lipids under bombardment by  $\text{Ar}^+$  ions. Essential influence of the method of target preparation from organic compounds on the yield of the excited particles is demonstrated. The processes resulting in formation of excited particles under ion bombardment of complex organic systems are specified. The model of interaction of lipids with organic dyes is proposed.

**Keywords:** ion-photon emission, excited particles, spectral composition, emission spectra, quantum yield of radiation, organic dyes.

## 1. Introduction

During the last decade the studies that joined two fields of science, rather far from each other, namely, electronics and biochemistry, were intensely developed. Their symbiosis stimulated the appearance of a new branch of science – bioelectronics (molecular electronics) [1]. One of the research methods of bioelectronics is the photodynamic therapy [2], based on local activation of a photosensitiser (PS) accumulated in a tumour, with the visible red light, which leads to the photochemical reaction that destroys the tumour cells. Organic dyes are typically used as PSs. However, the 'optimal' PS that would completely satisfy the requirements to this group of preparations is still not found [3]. The mechanism of photodynamic therapy is complex and not completely studied [3]. Therefore, the investigation of the processes that occur in the excited PS molecules, as well as the processes of dissolving PSs in solvents and the mechanisms of interaction of PSs with lipids, is an urgent problem. Its solution requires the development of high-sensitivity quantitative and semi-quantitative methods of diagnostics for organic structures at the atomic and molecular level.

The most widespread methods of such diagnostics are the methods of probing the surface with ions having the mean energy 20–40 keV [4–6]. Among these an important place is taken by the studies of ion-photon emission (IPE) that consists in knocking out the excited particles with subsequent emission of photons by them. Based on the IPE, the method

of ion-photon spectroscopy (IPS) is developed that provides simultaneous information about the nature and quantity of sputtered particles and about their kinetic energy, as well as determination of the character of the particle distribution over the excited states.

In the present paper the results of investigation of the basic characteristics of IPE (spectral composition, quantum yield and spatial distribution of the intensity of excited particles, escaping from the surface) are presented. The investigation was aimed at deeper understanding of the processes, occurring in complex organic systems under the interaction of beams of charged particles with their surface, as well as at getting information, necessary for developing specialised methods of analysis of organic structures.

## 2. Experimental setup

The studies were performed using the experimental setup described in [7]. The ion source provided a beam of argon ions with the energy 20 keV and the current density 10–20  $\mu\text{A cm}^{-2}$ . The target was placed inside the chamber so that the incidence angle of the ion beam with respect to the normal to the target surface was 45°. This position of the target provided the quantity of particles knocked out from the target close to the maximal value. The pressure in the chamber was  $(1–2) \times 10^{-4}$  Pa and did not change during the operation of the ion source. Radiation from excited particles, knocked out from the target surface by the ion beam, escaped via the chamber window and was focused by an achromatic lens onto the entrance slit of the radiation analysis and collection system. The geometry of radiation collection allowed determination of the total number of photons, emitted by the excited particles, leaving the surface. The emission spectra in the wavelength range 250–800 nm were recorded with a photoelectric system, operating in the photon-counting regime.

## 3. Results of the experiment and their discussion

In this paper we studied the possibility of applying the IPS method to the analysis of the processes, taking place in complex organic systems. As representatives of such systems the organic dyes were chosen whose structural formula contains Br atoms [bromthymol blue (BTB) and bromphenol blue (BPB)], Cl atoms [methylene blue (MB), rhodamine 6G (R6G) and neutral red (NR)], and the alkali metal atoms [methylene orange (MO), eriochrome black (EB) and eosin (EO)].

The results of numerous experiments with organic objects show that the process of their sputtering is largely affected by the chemical environment of the molecule in the sample [4]. In this connection the method of the sample preparation is of

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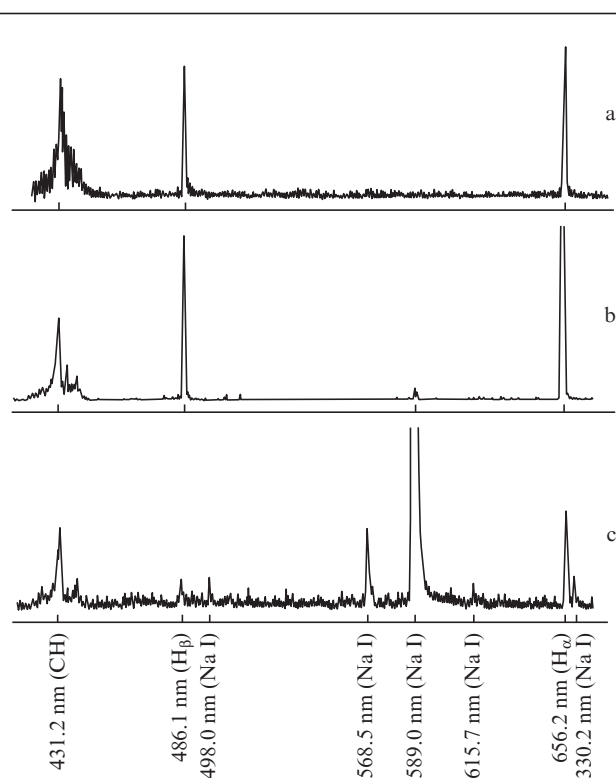
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great importance. At present a number of methods is used that can be divided into two groups, depending on the liquid or solid state of the target obtained. We studied both liquid and solid targets. In the first case the dye was dissolved in the liquid glycerol matrix. In the second case either a pellet was made from the dye powder, or the saturated solution of the dye was settled on a substrate and dried.

To achieve the formulated goals, the investigation of the IPE basic characteristics was carried out. For all studied samples the optical spectra of radiation of the excited particles were measured, from which the spectral composition and quantum yield of the radiation as well as the kinetic energy of the excited sputtered particles were found.

The study of the optical spectra of the excited particles, knocked out from the surface of organic compounds, was started from liquid targets, namely, saturated solutions of organic dyes (BTB, BPB, NR, MB, R6G, MO, EB) in glycerol.

Figure 1 shows the emission spectra of the excited particles, knocked out from the surface of glycerol and the solution of MO dye in glycerol. For comparison, the spectrum of excited particles, knocked out from the surface of a solid target, namely, a pressed pellet of the same dye, is also presented (Fig. 1c).



**Figure 1.** Emission spectra of excited particles, knocked out from the surface of glycerol (a), solution of MO dye in glycerol (b) and pressed pellet of MO (c). The line at  $\lambda = 330.2$  nm of Na atom is recorded in the second order of diffraction of the spectrometer diffraction grating.

The analysis of the obtained results shows that the optical emission spectra of the excited particles, sputtered from the surface of a liquid target, contains the lines of the emission spectrum of atomic hydrogen (Balmer series), the molecular band of CH radical and the weak lines of Na I spectrum (for dyes whose composition includes Na atoms). For all studied targets the calculation of the quantum yield of emission  $\gamma_\lambda$ , i.e., the number of photons at the studied wavelength per one incident  $\text{Ar}^+$  ion, was performed.

**Table 1.** Relative quantum yield of radiation of excited particles for liquid targets.

Target	$\gamma_\lambda$			
	430.9 nm (CH)	656.2 nm ( $\text{H}_\alpha$ )	486.1 nm ( $\text{H}_\beta$ )	588.9, 589.6 nm (Na I)
Glycerol	1 (1.1)	42.7	2.1	–
BTB	1 (4.5)	41	1.2	–
BPB	1 (3.4)	41	1.2	–
NR	1 (8.9)	26.3	1.2	0.3
MB	1 (2.4)	42	1.3	–
R6G	1 (3.6)	40	1.1	–
MO	1 (10.6)	45.3	2	0.4
EB	1 (11.9)	44	1.75	0.5

Note: the coefficients of transformation of relative values of the quantum yield into the absolute ones in the units  $10^{-6}$  photons per ion are given in parentheses.

Table 1 summarises the values of the quantum yield of emission for pure glycerol and the dye solutions with respect to the quantum yield of the emission of CH radical. It is seen that the relative quantum yields of the emission of the excited particles, entering into the composition of the hydrocarbon core of the dye, are practically the same for the emission spectra of glycerol and solutions of dye in glycerol, although the presence of dye in glycerol changes the absolute values of the quantum yield. The characteristic emission lines of Br and Cl atoms, entering into the composition of the corresponding dyes, are not observed. Besides, as follows from Fig. 1b and Table 1, even in the case of MO and EB dyes, containing easily excitable Na atoms, the lines of Na I spectrum in liquid targets are not practically observed.

The similarity of emission spectra of excited particles for dye solutions in glycerol and pure glycerol can be explained as follows. Being dissolved in glycerol, the dye molecule dissociates into charged parts, surrounded by glycerol molecules. The result is the appearance of micelles that shield the charged part of the dye molecule, in particular, the sodium atom. Therefore, in the spectrum we observe the radiation of the excited particles, knocked out from glycerol, and not from atoms, entering into the composition of the dye.

Thus, the obtained results have shown that the use of liquid targets for the study of complex organic systems using the IPS method is not reasonable.

Further investigations were carried out with solid targets, in particular, with dyes, whose composition includes the atoms of alkali metals, since they are easily excited and possess a rich spectrum in the wavelength region, recorded in the present paper (see the lines of Na I in Fig. 1c).

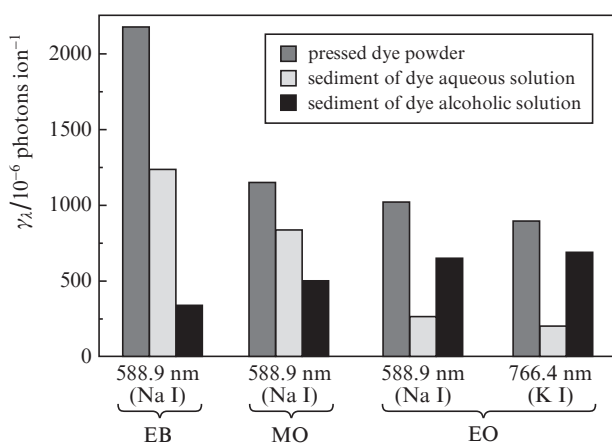
Two types of solid targets were studied: the pressed dye powder and dried sediments of saturated aqueous and alcoholic solutions of dyes. It was shown that for all types of targets the radiation of the CH radical is observed at the wavelengths  $\lambda = 430.9$  nm (Q-edge of the transition  ${}^2\Delta - {}^2\Pi$ ) and  $387.0$  nm (R-edge of the transition  ${}^2\Sigma - {}^2\Pi$ ), as well as that of excited hydrogen atoms at  $\lambda = 410.1$  nm ( $\text{H}_\delta$ ),  $434.0$  nm ( $\text{H}_\gamma$ ),  $486.1$  nm ( $\text{H}_\beta$ ), and  $656.2$  nm ( $\text{H}_\alpha$ ) of the Balmer series. Besides that there are a number of characteristic lines of the spectra of Na and K atoms that enter into the composition of the corresponding dyes. The most intense among them are the resonance doublets  $588.9$  and  $589.6$  nm (Na) and  $766.4$  and  $769.8$  nm (K). For the most prominent lines the emission quantum yield  $\gamma_\lambda$  was determined (Table 2).

Figure 2 presents the emission quantum yield for the alkali metal atoms for different types of targets. It is seen that the

**Table 2.** Quantum yield of emission of excited particles for solid targets.

Dye	Target	$\gamma_\lambda/10^{-6}$ photons ion $^{-1}$		
		430.9 nm (CH)	656.2 nm (H $\alpha$ )	486.1 nm (H $\beta$ )
MO	Pellets	5.5	33	3.3
MO	Sediment of aqueous solution	1.6	12	0.9
MO	Sediment of alcoholic solution	1.7	15	0.7
EO	Pellets	4.4	22	1.6
EO	Sediment of aqueous solution	4.8	22	1.6
EO	Sediment of alcoholic solution	3.3	15	1.2
EB	Pellets	2.6	15.4	1.8
EB	Sediment of aqueous solution	3.1	17.8	1.1
EB	Sediment of alcoholic solution	4.3	22.5	1.6

greatest value of  $\gamma_\lambda$  is observed at bombarding the pellet targets. For sediments of aqueous and alcoholic solutions of the studied dyes the value of  $\gamma_\lambda$  decreases individually for each dye. This can be explained as follows. In the course of dissolving the dyes in the solvent their molecules dissociate into ions, namely, the negatively charged ion of the core and the positively charged ion of the metal [8]. The degree of dissociation depends on both the dielectric constant of the solvent, which is 78.3 for water and 25.2 for alcohol, and the degree of solubility of the dye in the solvent. The EB and MO dyes are soluble in both solvents [9, 10]; therefore, only the ionising ability of the solvents affects the yield of excited particles, which is confirmed by the obtained results (Fig. 2). The EO dye is poorly soluble in water and well soluble in alcohol, and from Fig. 2 we see that although the ionising ability of alcohol is three times lower than that of water, the yield of excited atoms of alkali metals Na and K, entering into the EO composition, for alcoholic solution is higher, than for the aqueous one. This is, probably, associated with the different degree of EO solubility in these solvents.

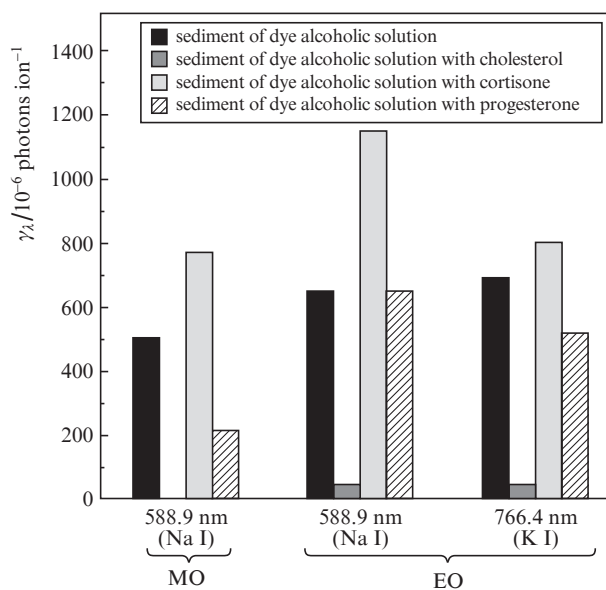
**Figure 2.** Emission quantum yield of the atoms Na and K for solid targets of the dyes EB, MO, and EO.

Thus, it is experimentally shown that the yield of excited particles under the ion bombardment of organic compounds is largely affected by both the ionising ability of the solvent and the degree of solubility of the compound in the solvent. This influence remains the same for the dried sediment of the corresponding solution.

Further studies were carried out for the mixtures of organic dyes with lipids. It is known [11] that the lipids are compounds

of biological nature that are solvable in non-polar solvents and cannot be dissolved in water. Lipids include fats, fat-soluble vitamins, steroids, etc. In the present work we studied cholesterol, cortisone and progesterone, belonging to the class of steroids. A specific feature of steroids is that they all possess a similar carbon skeleton. To classify steroids, use is made of the enumeration of carbon atoms in rigorously defined order [12].

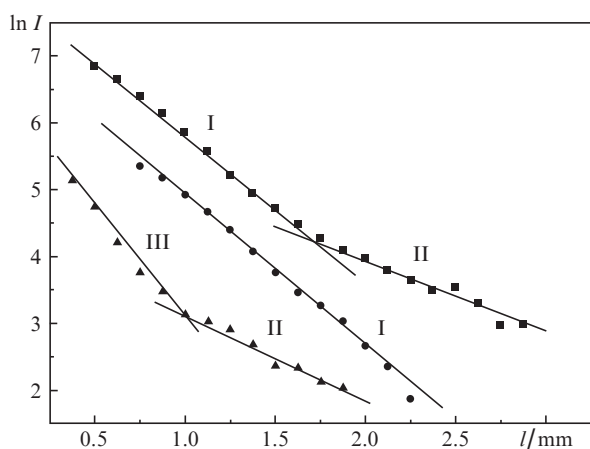
Figure 3 presents the emission quantum yield of the alkali metal atoms for dried sediments of saturated alcoholic solutions of MO and EO dyes in mixture with lipids. For comparison the data for sediments of alcoholic solutions of pure dyes is also presented. It is seen that in comparison with pure dye the dye-cholesterol system demonstrates significant, but different for each dye reduction of  $\gamma_\lambda$ , for the EO-cortisone mixture  $\gamma_\lambda$  increases, and for the EO-progesterone system  $\gamma_\lambda$  remains nearly the same, as for pure dye. As to MO, the value of  $\gamma_\lambda$  for the dye-progesterone system decreases, which is probably due to poor solubility of MO in alcohol. The comparison of  $\gamma_\lambda$  values for the major spectral lines of hydrogen atom (Balmer series) and CH radical has shown that the presence of lipids in the target leads to an insignificant increase in the quantum yield.

**Figure 3.** Emission quantum yield of atoms Na and K for solid targets of MO and EO dyes and their mixtures with lipids.

In the solution at the interaction of the dye with lipid the atom of metal can join the lipid molecule, but this largely depends on the presence and activity of the polar group OH in the lipid. In the case of cholesterol, where the OH group is located near the third carbon atom, the metal atom becomes surrounded by the cholesterol molecules, which reduces the probability of knocking the metal atom out by the ion beam. Due to this, the value of  $\gamma_\lambda$  for the emission of Na and K atoms decreases, and so does the number of the atoms knocked out. The presence of a very active group COCH<sub>2</sub>OH in cortisone may lead to the increase in the degree of dissociation of the dye in alcoholic solution. As a result, the yield of the excited alkali metal atoms grows as compared to the yield in the mixtures of dyes with other lipids. Progesterone has no OH group at all in its structural formula, and for dye-proges-

terone mixtures no changes in the spectra are observed as compared to the case of bombardment of the alcoholic solution of the pure dye.

The analysis of the spatial intensity distribution of emission of escaping excited particles allowed the estimation of their kinetic energy [13] and drawing a conclusion about the dynamic processes, leading to knocking them off. Figure 4 shows a typical dependence of the intensity of the resonance doublet of Na atom on the distance  $l$  from the surface of the target. It is seen that for dye pellet targets whose spectra are the most intense, the emission is observed from two velocity groups of Na atoms with the energy 100–150 eV (part I) and 700–1000 eV (part II). For sediments from alcoholic solutions of pure dye the emission is observed only from the first group of atoms in the case of low-intensity spectra (part I) or from both atomic groups in the case of more intense spectra. In the mixture of a dye with cholesterol, besides the high-energy atomic group (part II) a group of very slow particles appears having the kinetic energy 20–40 eV (part III). For mixtures of a dye with cortisone and progesterone the spatial intensity distribution is similar to that for the sediment from the alcoholic solution of a pure dye. The estimate of the kinetic energy of the knocked-out excited hydrogen atoms and CH radicals shows that the energy of these particles is independent of the type of the target. The hydrogen atoms are knocked out with the kinetic energy  $\sim 20$  eV, and the kinetic energy of the CH molecules is less than 1 eV.



**Figure 4.** Spatial intensity distributions of emission of excited Na atoms for solid EO target: dye pellet (■); sediment of dye alcoholic solution (●); sediment of dye alcoholic solution with cholesterol (▲).

The presence of different velocity groups among the excited particles is caused by the different processes of their release [14]. Small values of the kinetic energy (1–50 eV) indicate the appearance of an excited particle in the process of breakup of a large complex. Large kinetic energies indicate knocking out the alkali metal atoms by direct impact ( $\sim 300$ – $900$  eV) and as a result of cascade collisions ( $\sim 150$  eV).

#### 4. Conclusions

It is shown that the method of preparing the target from organic compounds essentially affects the yield of excited particles under the ion bombardment of targets.

The possibility is demonstrated to use the IPS method for investigating the processes that occur in complex organic systems. The most informative are the data, obtained in the analysis of emission spectra of the excited atoms of alkali metals that enter into the composition of organic compounds.

It is found that the sediment, obtained by evaporation of the organic compound solution, keeps the information about the processes that took place in the solution, which affects the yield of excited particles under the ion bombardment of targets.

A model is proposed for the interaction of lipids with organic dyes that explains the influence of lipids on the yield of excited particles under the ion bombardment of targets.

It is shown that the excited particles under the ion bombardment of complex organic compounds are produced both due to the processes of their direct knocking-out and because of breakup of a complex excited molecule.

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