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Luminescent studies of bisphenol A solutions under the action of the electron beam

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The results of measuring the luminescence of ambient air and solutions of an organic compound during their irradiation with a high-current pulsed electron beam with an average energy of $E_e = 170\,\mathrm{keV}$ and a duration of 2 ns, generated by the RADAN-303 accelerator, are presented. It is shown that, under such exposure, the transformation of dissolved bisphenol A occurs, which is accompanied by an increase in the absorption coefficient of the solution in the wavelength range of more than 300 nm and, as a consequence, a decrease in the intensity of air luminescence bands with an increase in the number of irradiation pulses. The results showed the degradation of the BPA solution to complete decomposition under the action of an electron beam treatment.

Keywords: electron beam, air, solutions of organic compounds, luminescence, absorption, decomposition.

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Introduction

In the world, on the one hand, electron beams are intensively used in various technological industries: in the synthesis of bisphenol-A-polycarbonate for the production of organic electronic devices, for photoconductivity during electron bombardment, in manufacture of sensitive and inexpensive capacitive sensors, in micronanofluidics, etc. At the same time, the mechanism of action of an electron beam of different intensity on dissolved organic compounds is still not fully disclosed. On the other hand, wastes, which usually contain substituted phenols, various organic compounds that harm the life of biological organisms, get into natural waters [1–4]. Water pollution by toxic stable compounds from chemical plants is a major concern around the world [1]. Traditional wastewater pretreatment technologies such as adsorption, coagulation, biochemical, electrochemical and enzymatic oxidation are often either ineffective or include partial degradation of dissolved toxic compounds with the formation of secondary pollutants. As a rule, schemes based on widespread biodegradation do not provide the degree of removal of all types of pollutants necessary for the organization of wastewater reuse. There is a serious question in the world community about the development of efficient and fast technologies for the elimination of toxic organic compounds from the environment. It is believed that it will be possible to cope with these problems only as a result of the large-scale application of new promising modern purification technologies [5].

An analysis of experimental works devoted to the decomposition of impurities of various simple compounds (NO, NO_2, CO etc.) in air under the action of a pulsed electron beam showed that the energy consumption for decomposition of these molecules is one of the lowest ($20-30\,\mathrm{eV}$ to break one bond of the molecule). This is due to the fact that when exposed to the beam, active centers — free radicals, ions or excited molecules — appear and conditions are formed that are favorable for the flow of chain processes [6–9] in the air.

The general physical principle of the organic molecules transformation in water under the action of UV radiation is that after absorption of a light quantum, the molecule goes into an excited state. This process takes a long time and is quite energy intensive. Pulsed electron beams, compared to UV radiation, are able to penetrate into deeper layers. The penetration depth of the electron beam depends on the beam energy and the nature of the material being irradiated. The study of luminescence of organic compound solutions under the action of an electron beam contributes to solving the problem of diagnostics and disposal of dissolved organic compounds, reducing the burden on the environment and the content of transformation products. The main aim of our study is to study decomposition of bisphenol A during and after exposure to a pulsed electron beam by optical absorption spectroscopy and luminescence. The results obtained correspond to the world level of research in the field of innovative technological schemes for water purification, which corresponds to modern challenges and ensures the relevance of the chosen topic. To the best of our

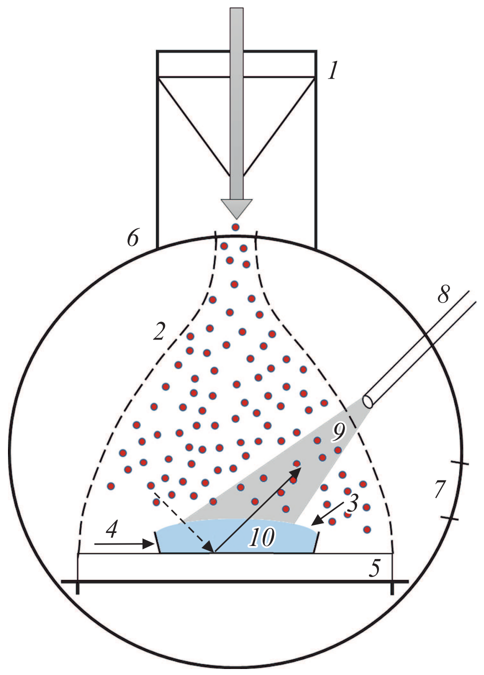

Figure 1. Unit layout: *1* — vacuum diode, *2* — electron beam, *3* — sample, *4* — cell of aluminum foil, *5* — holder, *6* — shielded chamber, *7* — door, *8* — light guide, *9* — luminescence detection area, *10* — direction of rays reflected from the cell bottom and entering the light guide.

knowledge, no work has been reported on the diagnostics of decomposition of dissolved bisphenol A by an electron beam using luminescent methods.

Procedure and methods

The objects of study were distilled water and a solution of 2,2-bis(4-hydroxyphenyl)propane (BPA) in it, which was synthesized by the commercial company Sigma-Aldrich (article Si-AlS8751-25G). This compound is slightly soluble in water; therefore, for its complete dissolution to concentration of 1 mM, a dry sample weight of BPA was placed in distilled water (pH 5.6), then it was placed in an ultrasonic mixer at temperature of 40°C for 2 h. The absorption spectra of the studied solutions were recorded on a Shimadzu UV-1700 spectrophotometer (Japan) at room temperature in the region of 200−1100 nm.

The spectral luminescence characteristics in the region from 200 to 800 nm of the air plasma above the surface of the liquid and the liquid itself were studied on a KLAVI [10] type unit. The liquid was irradiated with a pulsed electron beam with duration of 2 ns with average electron energy of 170 keV and electron current of 130 A. The number of irradiation pulses following with repetition rate of 1 Hz varied from 1 to 3200. Experimental unit layout is presented in Fig. 1.

The electron beam from the vacuum diode of the RADAN-303 nanosecond accelerator is emitted into the air medium of a metal chamber (with a volume of 1100 cm^3) perpendicular to the surface of the liquid solution. A liquid sample (distilled water or aqueous solution of BPA at concentration of 1 mM with a volume of 1 ml) in aluminum foil cell is placed on an apparatus table at a distance of 12 mm from the exit window of the vacuum diode. The thickness of the liquid layer was 2 mm. The diameter of the electron beam on the solution surface was 12 mm, the depth of electron penetration into the solution was — 100−150 μm. To record the spectrum of pulsed cathodoluminescence (PCL) excited in the irradiated zones of the solution and the air medium by beam electrons, the light flux was transmitted to the spectral device by a stranded quartz light guide with a bundle diameter of 1 mm. The light guide was directed to the center of the apparatus table. It was introduced into a metal chamber at an angle 45° to the direction of the electron beam at a distance of 5 mm from the center of the liquid surface, enclosing an ellipse 5×6 mm on the solution surface. The time-integrated luminescence spectrum in the range of 200−850 nm was recorded by two multichannel photodetectors with sensitivity ranges of 200−400 nm and 400−850 nm. The spectrum was averaged over 20 pulses. In this case, the instability of the amplitude parameters of the recorded averaged spectrum did not exceed 10%. Experimental studies were carried out in air at room temperature.

After irradiation with a given number of electron pulses, the irradiated solution was diluted to 1 : 10 with distilled water to record the absorption spectrum.

To diagnose decay of BPA in solution, a change in the spectrum and intensity of the volume radiation of liquid and air, localized near the solution surface and simultaneously excited by an irradiating electron beam, was recorded.

Results and discussion

Beam electrons expend their energy on excitation, dissociation and ionization of particles present in air and liquid. Active particles coming from the solution as a result of BPA transformation reactions under the action of a pulsed electron beam can change the air composition in the metal chamber, as well as the mechanism and composition of the BPA transformation products. The oxygen contained in the chamber air contributes to formation of reactive particles in the plasma formed by the electron beam, and can bind carbon to CO_2 and CO. For illustration, Figure 2 shows the luminescence spectra in the UV and visible regions recorded at different numbers of pulses of electron irradiation of distilled water and the background luminescence spectrum of air, measured with an empty cell in the chamber. In the UV range, three strong relatively narrow bands are recorded at 313.5, 335.9, and 356.6 nm. In the visible range, two weaker broad bands are observed with maxima approximately at 469 and 649 nm (Fig. 2, *b*). Bands at 313.5 and 356.6 nm are emitted by CO_2 molecules, the band at 335.9 and broad bands at 469 and 649 nm are emitted by

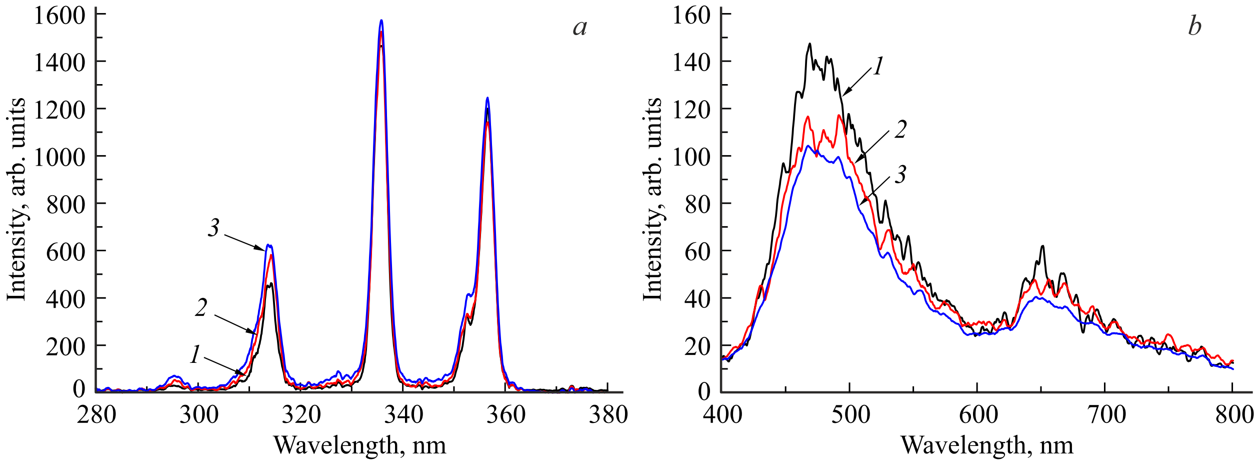

Figure 2. Spectrum of the background radiation of air with an empty cell (*1*) and with a cell filled with distilled water after preliminary irradiation with 50 (*2*) and 1600 (*3*) electron pulses: *a* — UV photodetector, *b* — visible range photodetector.

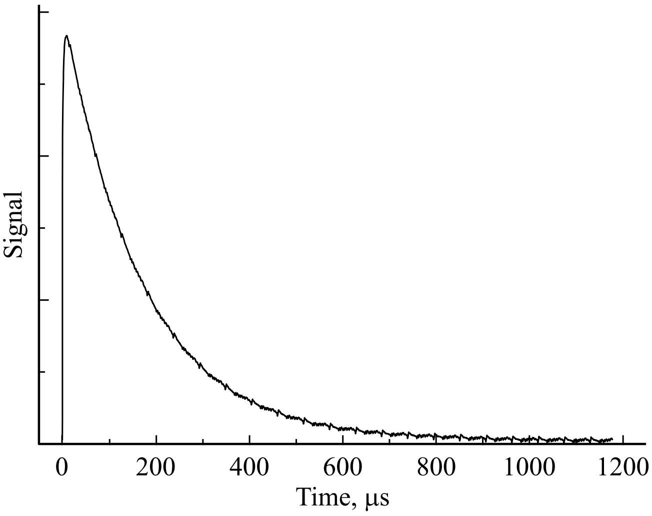

Figure 3. Intensity kinetics of the air emission band at 356.9 nm.

CN and CO [11] molecules, which are components of air plasma created by beam electrons.

The intensity kinetics of all bands is of the same type (Fig. 3) and is well described by the formula:

$$I(t) = I_0[\exp(-t/\tau_a) - \exp(-t/\tau_{d1}) - \exp(t/\tau_{d2})], \quad (1)$$

where I_0 — maximum intensity at $t = t_{\max}$, τ_{d1} and τ_{d2} — characteristic luminescence attenuation times, and τ_a — characteristic time of the kinetic instrumental function of the measuring system. The other parameters are listed in the table. It can be seen that the emission in all these bands is mainly of a recombination character.

The same bands remain in the luminescence spectra when distilled water and aqueous solution of BPA are introduced under the electron beam (Fig. 4). No new bands appear, i.e. distilled water and aqueous solution of BPA do not luminesce when irradiated with electrons, at least in the range of 200–850 nm. At the same time, in the luminescence spectra recorded in the presence of water upon irradiation with from 50 to 1600 electron pulses (Fig. 2), the change in the intensities of all bands relative to the background air glow does not go beyond the instrumental instability (less than 10%) arising due to the instability of the electron beam parameters. At the same time, in the luminescence spectra recorded in the presence of BPA solution, there is a noticeable decrease in the intensities of all bands (Fig. 4) relative to the background radiation of air. Moreover, with increase in the number of irradiation pulses from 50 to 3200, the reduction range increases. This fact correlates with an increase in the optical density of the solution in the spectral region of more than 300 nm with an increase in the number of irradiation pulses from 0 to 3200 (Fig. 5, insertion). Indeed, according to the scheme of the experiment (Fig. 1), the fraction of air radiation reflected from the cell bottom, falling into the receiving cone of the light guide, is $\delta_r = 1 - I_d/I_m$, where I_d — value, constant for a given geometry of the experiment, equal to the intensity of the direct radiation of the air entering the receiving cone of the light guide and not interacting with the solution, I_m — the measured intensity. If the absorption index of the solution is equal to $\alpha(\lambda)d$ (d — thickness of the solution layer), then the fraction of radiation reflected from the cell bottom decreases by $\exp[-2\alpha(\lambda)d]$ times. Thus, the decrease in the intensities

Kinetic parameters of air luminescence bands

λ, nm	τ_{d1}, ns	τ_{d2}, μs	τ_a, μs
315	51.9 ± 11.0	2.41 ± 0.27	169.17 ± 0.63
336	80.7 ± 11.5	2.73 ± 0.12	167.59 ± 0.21
356.8	57.2 ± 12.5	2.40 ± 0.04	168.12 ± 0.21
469	40.5 ± 16.4	2.66 ± 0.36	198.00 ± 2.90

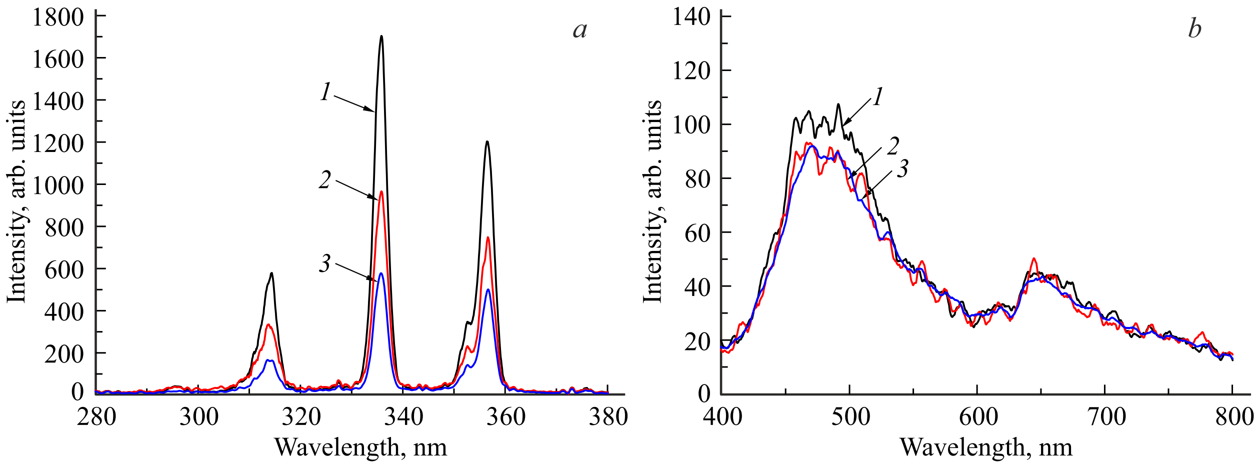

Figure 4. Air background radiation spectrum with an empty cell (*1*) and with a cell filled with BPA solution after preliminary irradiation 50 (*2*) and 1600 (*3*) with electron pulses: *a* — UV photodetector, *b* — visible range photodetector.

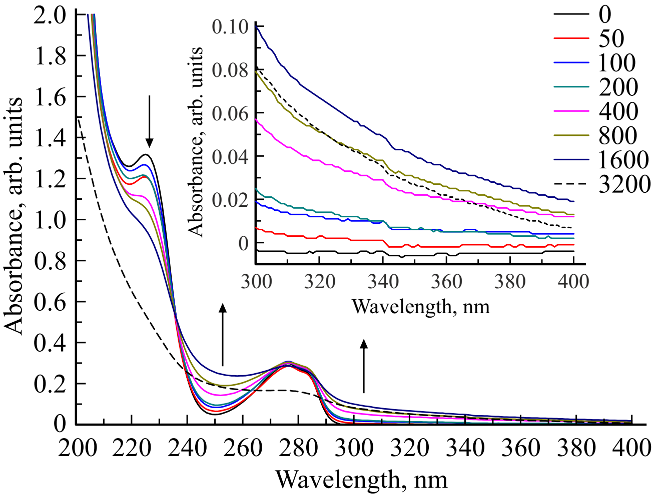

Figure 5. Absorption spectra of aqueous solutions of BPA after preliminary irradiation with 50 and 3200 electron pulses. The arrows indicate the direction of change in the intensity of the bands.

of the emission bands of air in the presence of aqueous solution of BPA is associated with absorption of a part of the radiation, entering the receiving cone of the light guide, by the solution.

As can be seen in the scheme of the experiment (Fig. 1), the direct radiation of the air plasma and the radiation reflected from the cell bottom and twice passing through the solution enter the luminescence detection cone. As a result of BPA transformation reactions under the action of an electron beam, the composition of the solution and its absorption coefficient change. This process manifests itself in the form of a decrease in the intensity of the air luminescence bands relative to the background value due to the partial absorption of the air radiation, reflected from the cell bottom, by the BPA solution. Based on the data in Figs 4 and 5, it can be argued that under the action of electron beam irradiation, an intense transformation of the BPA organic compound in water occurs. Decrease in the intensity of the bands (Fig. 5) in the region of 230 nm and increase in the region of 250 and more than 300 nm indicates the active degradation of BPA and formation of transformation products under the action of an electron beam. A weak change in the intensity of the bands in the region of 270–280 nm indicates that phenols [12] of various structures are accumulating in the solution, which are supposed products of BPA decomposition. The curve at 3200 pulses proves complete degradation of the substance under study.

The processes of BPA transformation in water under irradiation with an electron beam with a duration of 2 ns with average electron energy of 170 keV and current density of up to 130 A/cm^2 occur both due to electrons that penetrate into the solution to a depth from 100 to 150 μm, and due to the X-ray bremsstrahlung generated by the electron beam, penetrating to depth of more than 2.0 mm. Thus, the effect of an electron beam on BPA solution is of a volumetric character, and the transformation of BPA molecules occurs mainly due to the breaking of molecular bonds by fast beam electrons. Indeed, the complete decomposition of BPA occurs after irradiation with $N = 3200$ electron beam pulses. The fluence of each pulse is $N_e = i_e t_e / e_0 \approx 1.6 \cdot 10^{12}$ of electrons with energy $E_e = 170$ keV incident on 1 cm^2 of the solution surface. These electrons, penetrating into the solution, carry out $N_m = N N_e E_e / \varepsilon \sim 2.9 \cdot 10^{20}$ breaks of molecular bonds, the number of which approximately coincides with the number of BPA molecules in the solution. Here $i_e = 130$ A/cm^2 — electron current density, $t_e = 2$ ns — its duration, e_0 — elementary charge, $\varepsilon = 30$ eV — energy expended by fast electrons to break one bond. We assume that under such an effect, BPA in solution will undergo transformation due to formation of solvated electrons and reactive oxidants in solution. It can also be assumed that the BPA transformation can occur through highly excited electronic states. However, this assumption is not confirmed by experiment, since the luminescence spectrum does not contain BPA singlet-singlet fluorescence bands even in the region of 280−300 nm.

Conclusion

It has been shown that water and aqueous solution of BPA do not luminesce under the action of an electron beam.

Degradation of BPA under the action of an electron beam has been established, which manifests itself in a change in the optical density of the solution in the BPA absorption spectra, as well as in increase in the absorption of air spectral lines by the BPA solution with increase in the number of radiation pulses.

Attenuation of the air spectral lines during BPA degradation can be used to qualitatively determine the degree of degradation of dissolved organic matter in real time.

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Conflict of interest

The authors declare that they have no conflict of interest, financial and other conflicts.

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