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GENERATION OF LEADING CENTERS IN THE BELOUSOV-ZHABOTINSKY REACTION BY 30 MeV ALPHA BEAM

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Generation of leading centers in the Belousov–Zhabotinsky reaction by a 30 MeV alpha beam

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Annotation: Results of the observation of the generation of leading centers in the Belousov–Zhabotinsky reaction under the action of a 30-MeV alpha beam from the cyclotron in SINP MSU are presented. Observations were performed for two configurations of the cell: planar and capillary. Threshold values of the absorbed dose for the generation and complete quenching of autowaves were estimated.

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Инициация ведущих центров в реакции Белоусова-Жаботинского под действием пучка альфа-частиц с энергией 30 МэВ

Препринт НИИЯФ МГУ-2006-6/805

Аннотация:
Приводятся результаты наблюдения возникновения ведущих центров в реакции Белоусова-Жаботинского под действием пучка альфа-частиц с энергией 30 МэВ из циклотрона НИИЯФ МГУ. Наблюдения выполнены для двух конфигураций кювет: плоской и капилляра. Оценены величины пороговых значений поглощенной дозы для возникновения и полного гашения автоволн.

The version in Russian is presented in http://dbserv.sinp.msu.ru:8080/sinp/files/pp-797.pdf

Table of contents

Introduction

It is known that some effects in chemical autooscillatory reactions in homogeneous media can model many self-organization processes in living systems. Evidently, these effects are a substantial part of such phenomena as pulse propagation in excitable media, "biological clock", intracell division control, muscle contraction, and others /1, 2, 3/. Thus, when a homogeneous medium with a chemical oscillatory reaction is subjected to an external impact, we can model and, to some extent, predict the result of this impact on biological systems.

In our previous studies, we used autooscillatory reactions for modeling the effect of factors /4/ that occur in some fields of human activity (increased pressure, electromagnetic fields, ionizing radiation, etc.).

In this work, we consider the effect of charged particle beams with high linear energy transfer (LET) on the Belousov–Zhabotinsky (B–Zh) reaction.

Experimental

As known /5, 6/, the B–Zh reaction is an autooscillatory reaction with excitable kinetics (Fig. 1). In this reaction, Ce^{4+} ions interact with malonic acid and are reduced to Ce^{3+} (*I*):

$$CH_2(COOH)_2 + Ce^{4+} \longrightarrow Ce^{3+} + P$$

The Ce^{3+} ion formed in this reaction must further enter into the reaction with the bromate ion (*II*), which leads to the stationary distribution of cerium between the oxidation states. However, this reaction is autocatalytic, and the self-accelerating mode is preceded by an induction period. The reaction is switched on not immediately, and, therefore, during the induction period nearly all Ce^{4+} ions are transformed into Ce^{3+}. The light-yellow color of the solution, which is caused by light absorption in the visible region by the Ce^{4+} complex, disappears. After the end of the induction period, self-accelerating rapid transformation of Ce^{3+} ion to Ce^{4+} occurs, and the solution is colored again. In other words, until all Ce^{4+} is not transformed into Ce^{3+}, the latter does not begin to oxidize. Thus, the reaction proceeds for some time, next stops, next begins again, and so on until all initial reactants are consumed.

The periodic character of the process is explained as follows. Reaction (*I*) yields bromide ions, which retard reaction (*II*). However, the concentration of bromide in the system depends on the rate of the reaction in which bromide is consumed because of the interaction with bromate. If the concentration of bromide is

sufficiently high, reaction (*II*) stops, because Ce^{4+} is not regenerated in the oxidation of Ce^{3+} by bromate, and, as a result, the catalytic cycle is interrupted. When the concentration of Ce^{4+}, which decreases as a result of reaction (*I*), reaches the minimum possible value, the concentration of Br^- begins to sharply decrease. Then reaction (*II*) significantly accelerates, and the concentration of Br^- begins to rapidly increase thus retarding reaction (*II*). Then the entire cycle is repeated.

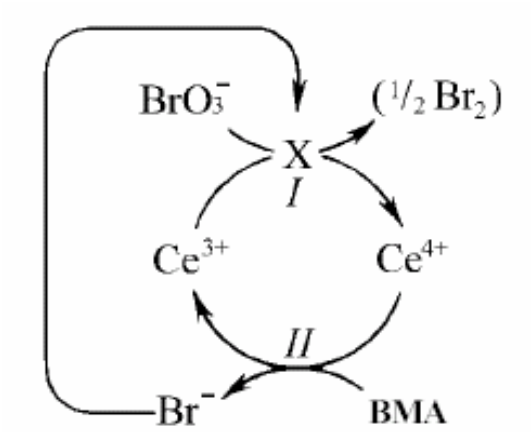


Fig. 1. Scheme of the Belousov–Zhabotinsky reaction.

In this work, we consider the effect of charged particle beams with high linear energy transfer on the Belousov–Zhabotinsky reaction. In particular, this factor occurs in outer space.

For the irradiation of samples, we used an alpha-beam from the 120-cm cyclotron at the Institute of Nuclear Physics, Moscow State University. Ferroin, the complex of Fe(II) with phenanthroline (phen), was used as the catalyst instead of Ce^{4+}. This catalyst was selected because ferroin has bright blue color and changes it to red on the transition Fe(II) → Fe(III), which allows the visualization of the process dynamics. Generally, the participation of ferroin in the process can be described by the following reaction:

$$6\,[Fe(phen)_3]^{2+} + 6H_30^+ + BrO_3^- \longrightarrow 6\,[Fe(phen)_3]^{3+} + 9\,H_20 + Br^-.$$

The schematic diagram of the setup in presented in Fig. 2. The alpha-beam from cyclotron (1) passed by the ion guide (4) through quadrupole lenses (2), deflecting magnet (3), protective wall (5), and further through the system of diaphragms (7) and a vacuum valve (6), went into air from the window (8) of the ion guide, and arrived to a working cell or a capillary (10). As the window at the edge of the ion guide, we used aluminum foil with the thickness of 50 μm. In some experiments, the beam was collimated with an additional replaceable diaphragm (9) of different configurations. This diaphragm was mounted on a rod moving with a micro engine, which allowed the remote control of the introduction and removal of the

diaphragm (or interception of the beam).

The diameter of the round diaphragm was 2 mm; the slit width was also 2 mm. The diaphragm was made of tantalum because induced radioactivity in it is low because of the high Coulomb barrier.

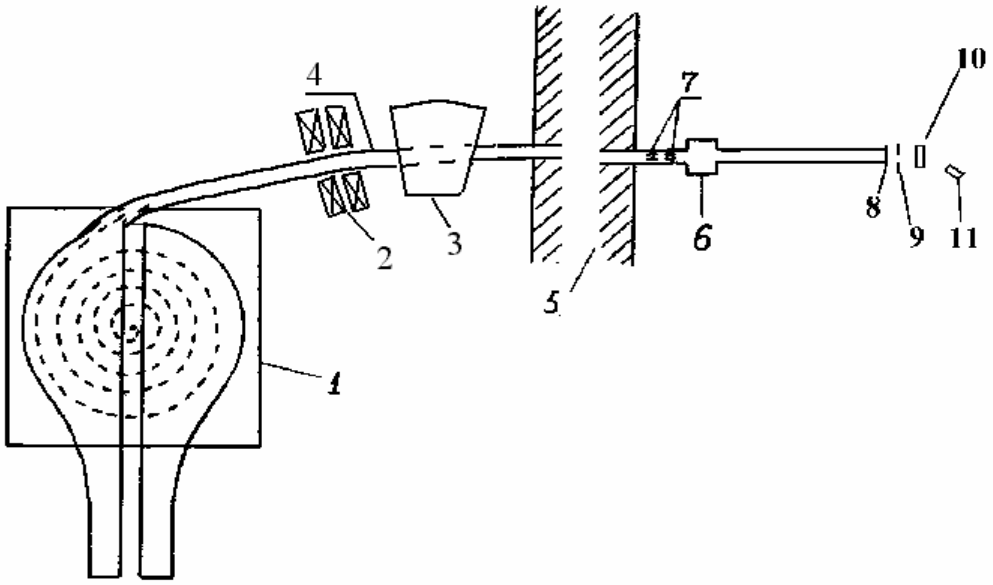


Fig. 2. Schematic diagram of the setup: (1) cyclotron, (2) quadrupole lenses, (3) deflecting magnet, (4) ion guide, (5) protective wall, (6) vacuum valve, (7) diaphragms, (8) ion guide window, (9) replaceable diaphragm, (10) working cell or capillary, (11) web camera.

Image acquisition of the process was performed with a Philips web camera (11) and a computer, which was connected to the camera through three USB repeaters arranged in series with a total length of 15 m. The image was recorded to the hard disk of the computer in the on-line mode. Then the color in analyzed points was decomposed into RGB components in the off-line mode using the color capture program. The results were used for the quantitative analysis of autowave processes. The arrangement of some elements of the setup is shown in more detail in Fig. 3.

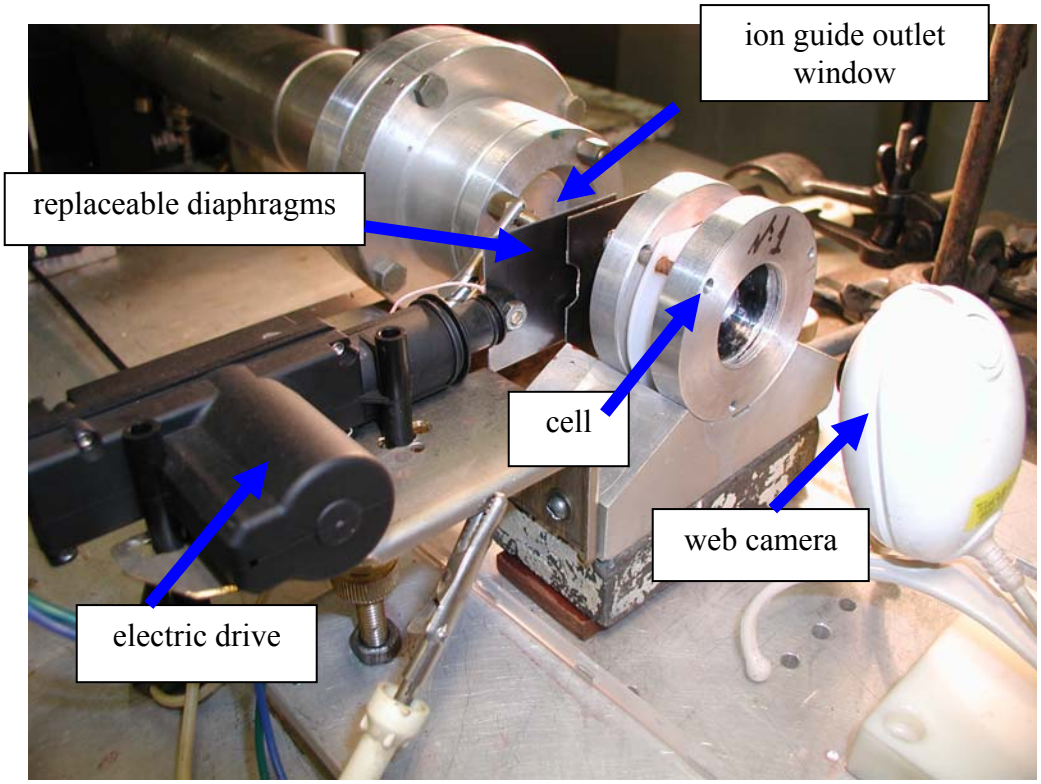


Fig. 3. Setup (photo).

The beam was monitored by varying the value of the charge at the diaphragm and the cell, which were isolated from the earth. A current integrator with a sensitivity of 2×10^{-4} μC/pulse and a scaler were used. To improve the uniformity of charge density of the accelerator over the window area, the beam was somewhat defocused with magnetic quadrupole lenses of the cyclotron and periodically controlled using a scintillation screen. The accuracy of the determination of absorbed dose was estimated at 30%.

The action of a cyclotron alpha-beam on the B–Zh reaction was studied at two geometries: planar two-dimensional and one-dimensional. In the first case, we used a special duralumin ring-shaped cell with the outer and inner diameters of 60 and 20 mm, respectively, and a thickness of 30 mm. In the central part of the cell, the reaction mixture was placed between two mylar films with a thickness of 20 μm tightened at the inner part of the cell ring. The gap between the films was from 0.8 to 1.0 mm. The cell was filled with a solution with a syringe through a special hole and placed behind the window of the ion guide at a distance of 5–7 cm.

In the second case, a Pyrex capillary with a length of 90 mm and outer and inner diameters of 1.2 and 0.9 mm, respectively, were placed instead of the cell. The capillary was located in the horizontal plane perpendicularly to the beam.

Energy losses of alpha particles in the window of the ion guide and in the air layer were 4.3 MeV, and the energy of alpha particles at the outer surface of the mylar film or capillary was 26.2 MeV. LET of alpha particles with this energy is about 6 keV/(μm of water) and decreases with particle slowdown in the solution. The radiation quality coefficient was 2 and above.

The energy of alpha particles arriving at the reaction mixture varied from 18.5 MeV at the capillary axis to 5.5 MeV and lower at the edges because particles passed the Pyrex layer of different thickness. LET of alpha particles at the end of the path was up to 2×10^{1} keV/(μm of water).

Thermal convection and diffusion during the experiment both in the chamber and in the capillary can be neglected.

Results and discussion

On the irradiation of the solution in the cell with the diaphragm 2 mm in diameter, concentric waves centered at the irradiated portion of the solution were initiated (Fig. 4), and the process of the formation of the wave front was repeated several times even after the end of the irradiation. The time of irradiation and the intensity of the beam were varied in the range from 1 to 60 s and 1 to 30 nA, respectively. The ratio of bromine and malonic acid (MA) in the solution was also varied (from 1 : 1 to 1 : 10). It was found that the most stable wave initiation corresponded to the ratio of these components of 1 : 6 and was nearly independent on the intensity of the beam. In Fig. 4a, spontaneous waves over the entire area of the cell and the formation of the first concentric wave around the slit are seen. Fig. 4b shows a clear concentric wave (second after the end of irradiation) and the trail of the first wave, and Fig. 4c shows the third (after the end of irradiation) wave and trails of the second concentric wave (corresponding video record of the process is presented in Appendix 1).

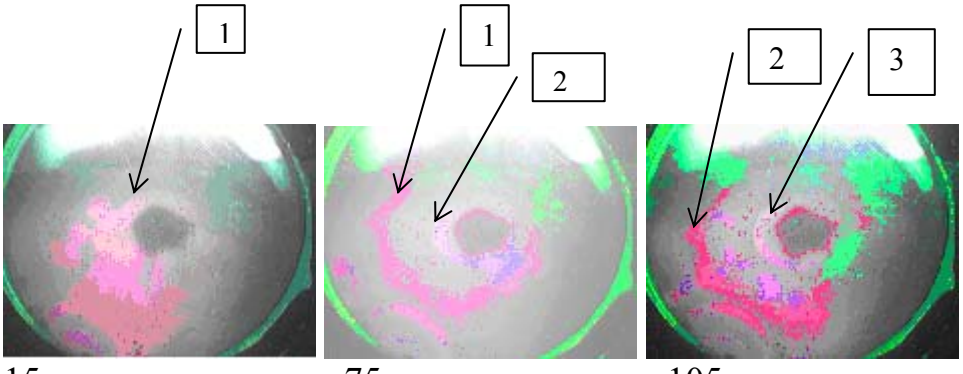


Fig. 4. Wave initiation in the cell with the round diaphragm. Initial concentrations of compounds (M): [MA] = 0.6, [$NaBrO_3$] = 0.1, [$Fe(phen)_3$] = 5×10^{-5}, [H_2SO_4] = 1.5

(the time from the beginning of irradiation is shown in the figures; the color of the solution is distorted).

When the slit diaphragm was used (Fig. 5), the front of the initiated wave replicated the shape of this diaphragm and had the form of two diverging planar waves. After the end of irradiation, the formation of two or three additional waves of the same shape but with lower intensity was observed (corresponding video record of the process is presented in Appendix 2).

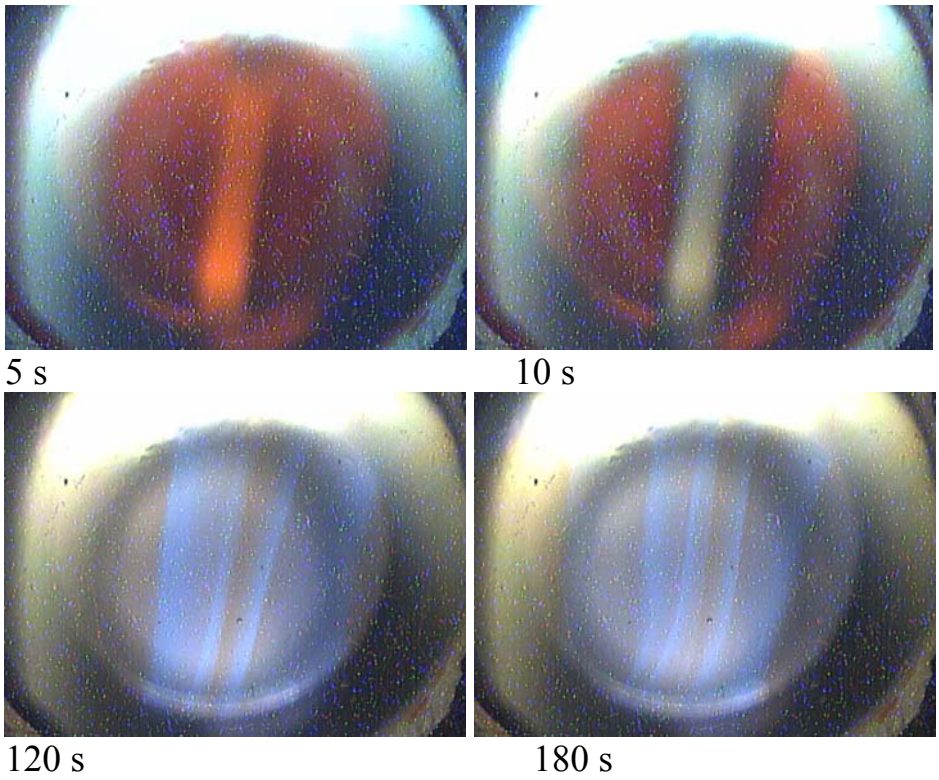
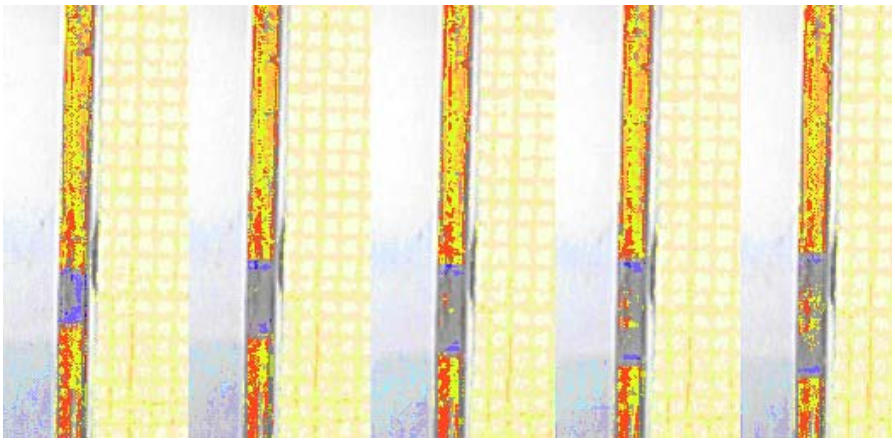


Fig. 5. Wave initiation in the cell with the slit diaphragm. Initial concentration of compounds (M): [MA] = 0.3, [$NaBrO_3$] = 0.1, [$Fe(phen)_3$] = 5×10^{-5}, [H_2SO_4] = 1.5 (the time from the beginning of irradiation is shown in the figures).

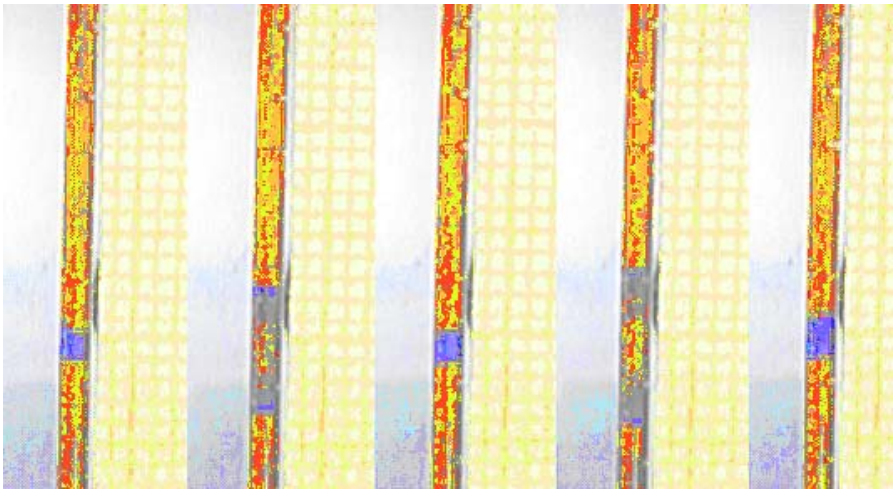
The most stable formation of the leading center was observed on the irradiation of the solution in the capillary (Fig. 6). In this case, two nearly planar waves diverged in opposite directions from the center of irradiation. The minimum value of the absorbed dose at which the formation of the leading center was observed was estimated at 8×10^{1} Gy. It should be noted that in this case the energy distribution of alpha particles in the solution not only was nonuniform in depth, but also depended on the place of their arrival at the surface of the capillary (corresponding video record of the process is presented in Appendix 3).

The superposition of the waves induced by the beam with the spontaneous waves, which commonly occur in the solution, resulted in their mutual cancellation.

Figure 7 presents the time-base sweep of the blue component of the RGB resolution in the point separated by 10 cm from the center of irradiation. In the figures, arrows indicate time intervals corresponding to the irradiation of the cell. In the figures, it is seen that the frequency of wave generation in the considered point depends on the geometry of the reaction volume and the shape of the diaphragm.



0 s 5 s 10 s 15 s 20 s



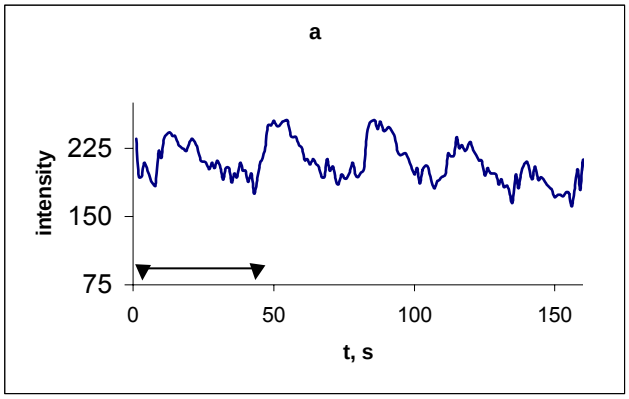
128 s 148 s 265 s 305 s 402 s

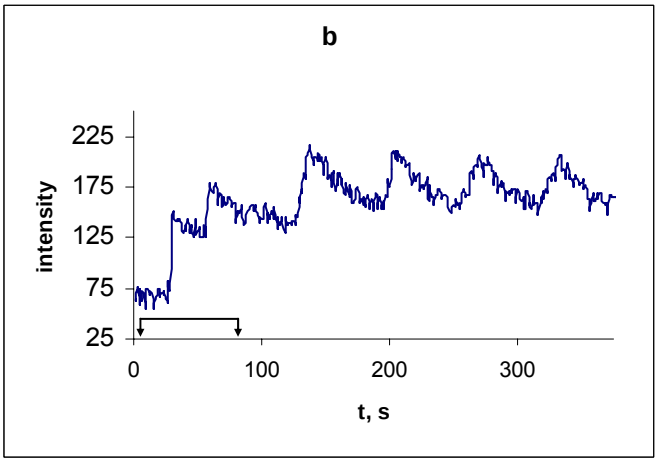
Fig. 6. Wave initiation in the capillary. Initial concentration of compounds (M): [MA] = 0.0048, $[NaBrO_3] = 0.0036$, $[Fe(phen)_3] = 5\times10^{-5}$, $[H_2SO_4] = 0.3$ (the time from the beginning of irradiation is shown in the figures; the color of the solution is distorted).

The interval between passing two repeated waves is about 35 s in the cell with the diaphragm in the form of a round window, about 65 s in the cell with the slit diaphragm, and about 100 s in the capillary. The dependence of autooscillations on the shape of the reaction volume is evidently related to the radical nature of the

processes that occur in the reaction mixture. It should be also noted that the intensity of waves after single irradiation decreases with time.

On the irradiation of the entire volume of the reaction mixture in the cell with the alpha beam at doses of about 60 kGy, the autowave process stopped in the entire volume of the cell (Fig. 8). After the end of irradiation, the autowave process restarted within 2–3 min (corresponding video record of the process is presented in Appendix 4). As known, a similar situation is observed on the continuous addition of Br^- anions to the system. Thus, it can be assumed that high-LET ionizing radiation activated the reaction of the reduction of bromate ions to bromide anions. This conclusion is confirmed in part by the change in color on the irradiation of the acidic solution containing potassium bromate and ferroin form blue to red and the return to the initial color after the end of irradiation (ferroin is an indicator of redox processes).





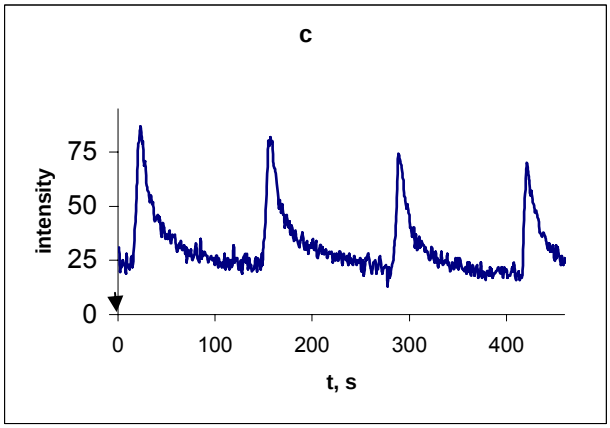


Fig. 7. Time-base sweep of the blue component of the RGB resolution in the point separated by 10 cm from the center of irradiation; (a) for the cell with the diaphragm in the form of a round window, (b) for the cell with the slit diaphragm, and (c) for the capillary. Arrows denote the beginning and the end of irradiation.

Only two experiments were described in the literature, where the irradiation of the B–Zh reaction with hard ionizing radiation was considered and its influence on autooscillatory processes was studied /7, 8/. In these experiments, Co^{60} gamma-radiation was used, and the entire reaction volume was irradiated. Even if the leading centers were generated on this irradiation (although this is improbable because of low LET values), these centers immediately quenched each other and could not be

observed. In these works, only the suppression of autooscillations under the action of gamma irradiation was observed.

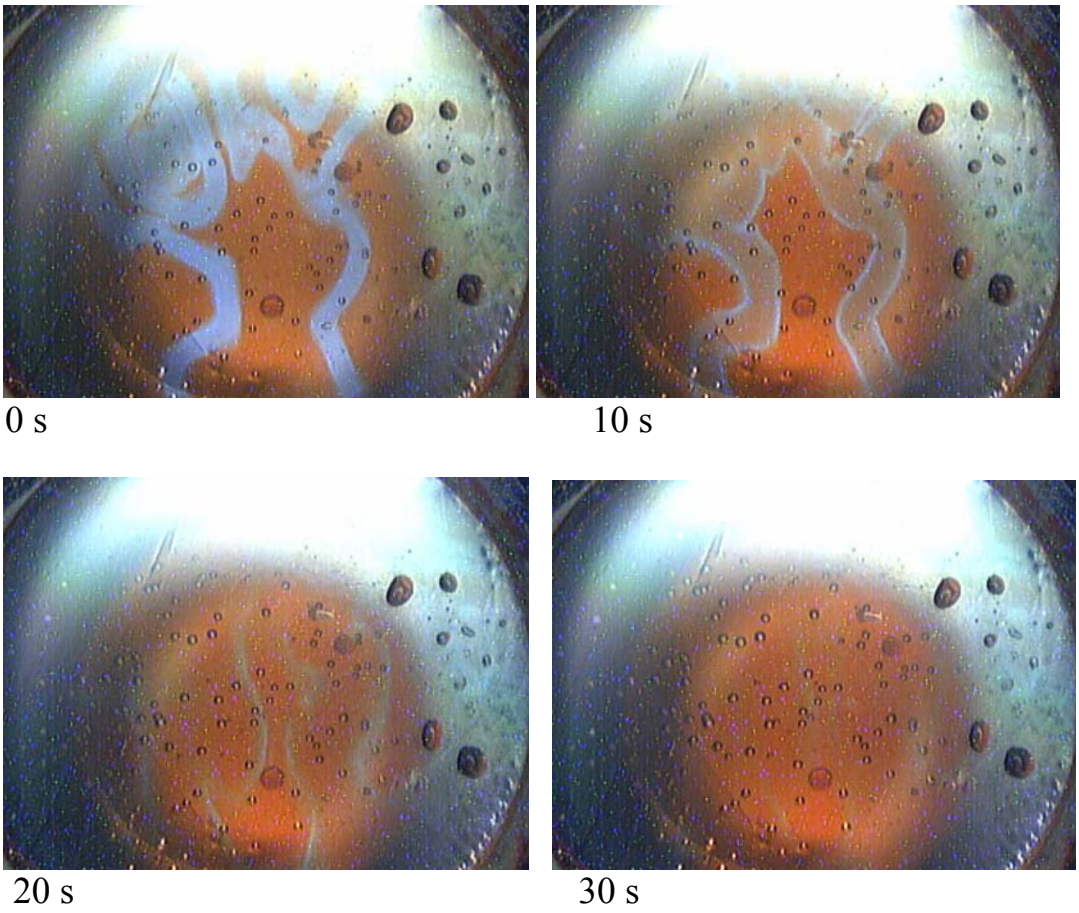


Fig. 8. Disappearance of autowaves under the action of hard radiation [1]. Initial concentration of compounds (M): [MA] = 0.004, [$NaBrO_3$] = 0.1, [$Fe(phen)_3$] = 5×10^{-5}, [H_2SO_4] = 1.5 (the time from the beginning of irradiation is shown in the figures).

The generation of new leading centers can be a result of radical reactions initiated under the action of hard radiation. In /9/, the initiation of the reaction

$$^{\bullet}O_2CH(CO_2H_2) + CH_2(CO_2H)_2 \Rightarrow HO_2CH(CO_2H)_2 + {}^{\bullet}CH(CO_2)H_2$$

was observed in the studies of the radiolysis of malonic acid under the action of a high-energy electron beam. In the opinion of the authors of /9/, this process can play

[1] Dots in the photograph are gas bubbles. Chromatographic analysis demonstrated the presence of a mixture of hydrocarbons in the composition of the gas, which can indicate that free-radical processes occur in the system.

an important role in the B–Zh reaction. In our opinion, this reaction can also cause the generation of new leading centers.

Conclusions

Thus, the generation of leading centers in an oscillatory reaction of the B–Zh type under the action of collimated radiation with high linear energy transfer was observed for the first time. Complete quenching of autowave processes under the action of total irradiation of the reaction volume was also observed. Along with their fundamental importance, the observed effects can be used for modeling processes of the radiation injury of living systems under the action of the radiation of this type.

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Appendix 1- p1.avi, 320×240, XviD MPEG-4, 2.67 MB.
Appendix 2- p2.avi, 320×240, XviD MPEG-4, 3.05 MB.
Appendix 3- p3.avi, 320×240, XviD MPEG-4, 3.36 MB.
Appendix 4- p4.avi, 320×240, XviD MPEG-4, 0.57 MB.

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Инициация ведущих центров в реакции

Белоусова-Жаботинского под действием пучка

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