

# Effect of Spark Discharge Plasma on Water, Physiological Saline, and Hanks' Solution

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**Abstract**—The effect of the duration of a current pulse of spark discharge in air on the composition of products formed in liquid both by the action of plasma radiation and with the participation of species formed in the discharge itself has been studied. The products formed in water, 0.9% NaCl, and in Hanks' solution have been determined. It has been that in all the cases, nitrous acid is one of the primary products. The yield of nitrous acid is the same in all the three solutions. With a decrease in the current pulse duration, the influence of the species formed in the discharge itself on the yield of nitrous acid increases. The products formed in water decompose within up to 13 days. Peroxynitrite and  $N_2O_3$  were identified as degradation products.

**Keywords:** spark discharge in air, current pulse duration, nitrous acid, water, 0.9% NaCl, Hanks' solution,  $N_2O_3$ , peroxynitrite

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## INTRODUCTION

The possibilities of using plasma in medicine are widely discussed [1]. The direct effect of an argon plasma jet and the use of secondary active species generated by plasma are considered [2]. In [3, 4], we addressed the formation of primary active species in water by the action of spark discharge plasma in air. The plasma radiated like a heated black body. Active species formed in the discharge itself, reaching the surface of liquid, can also contribute to the yield of active species, but this contribution was small under the conditions specified [3, 4].

The processes occurring in the discharge depend on the electric field strength in the spark gap. In the first stage of the discharge at the current pulse leading edge (0.1–0.2  $\mu$ s), the field strength is maximal and excited molecules and radicals are most likely to be formed. In the second stage during the current decay ( $\sim 150$   $\mu$ s), the discharge transforms to the arc. Stable species are formed from the radicals generated in the first stage. The radicals themselves decay at their generation site. Therefore, the main contribution to the formation of active species in water was made by plasma radiation. With a decrease in pulse duration, the yield of radicals formed in the first stage remain unchanged and the decay of radicals decreases in the second stage of the discharge when neutral species are formed from them. Therefore, the role of radicals produced in the discharge itself should increase with a decrease in current pulse duration.

The neutral products formed in the discharge in the second stage include nitrosamines identified by the UV absorption spectra of the treated water samples (a broad peak with a maximum at  $\lambda \sim 360$  nm), and by the IR spectra of the solid products [3]. In [4], a discharge was used with a pulse width of 150  $\mu$ s. Therefore, it is of interest to consider the change in the composition of the active species at a strong decrease in the duration of spark discharge current pulse.

The methods for generating active species considered in [3, 4] can be used in biological research. Biological objects (in particular, cells) die in clean water. Studies of objects of this kind are carried out in physiological saline (0.9% NaCl in water) or in Hanks' solution. Therefore, it is of interest to consider the effect of plasma radiation on these solutions. The purpose of this work is to study primary active species generated in water, physiological saline, and Hanks' solution by the action of both air spark discharge plasma radiation and the products formed in the discharge itself, as the duration of the discharge current pulse decreases.

## EXPERIMENTAL

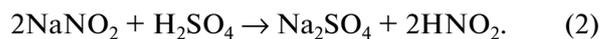
An IR50 generator of spark discharge plasma radiation, similar in design to the generator applied in [4], was used, but the discharge capacitor capacitance  $C$  was reduced from 3300 to 680 pF. At a value of  $C = 3300$  pF, the front duration was 0.1–0.2  $\mu$ s and the total duration of the current pulse was  $\sim 150$   $\mu$ s [4].

The pulse duration is determined by the time of charge dissipation in the spark gap. At  $C = 680$  pF in the generator used in this study, the current pulse duration was 5–6  $\mu$ s with the same front duration. The capacitor was charged via a ballast resistor of 6 M $\Omega$  from a power supply of  $V = 11$  kV. The capacitor was connected in parallel to a 2.5-mm discharge gap; the breakdown voltage of the gap was  $\sim 6$  kV. The discharge electrodes were made of a stainless steel rod of 2 mm in diameter. When high voltage was applied, a self-sustained spark discharge with a pulse repetition frequency of 50 Hz was formed. The energy released in the discharge was 0.6 J/s. The discharge cavity was closed with a fluoroplastic lid with a hole of a 20 mm diameter, through which the cavity communicates with a sample of treated liquid. That is, the liquid sample is exposed to the action of both plasma emission and the products formed in the discharge. In a separate experiment, the hole was covered with a quartz glass 2.3 mm in thickness. In this case, the contact of the gas in the discharge cavity with the liquid sample subjected to treatment was completely eliminated. The transmittance of the glass in the wavelength range from 200 to 800 nm was no less than 70%, i.e. the attenuation of the radiation flux was insignificant.

Liquid samples were treated in Petri dishes of 40 mm in diameter, the volume of the samples was 5 mL. The distance between the sample surface and the discharge electrodes was 30 mm. The sample treatment time was varied from 1 to 60 min. After the treatment, the samples were stored in closed containers for up to 13 days. The pH of the liquid was measured immediately after the treatment and on the following day, the absorption spectra of the sample were measured immediately after the treatment and every 24 h for 13 days. The UV absorption spectra were recorded with an AKVILON SF-102 spectrophotometer (Moscow, Russia). The optical path length of the cell was 10 mm. Absorbance  $A = \log(I/I_0)$  (D) was measured with respect to distilled water. The pH was measured with an Eksper-001 instrument (EKONICS, Russia). Reagent grade chemicals, sterile Hanks' solution, freshly prepared physiological saline (0.9% NaCl in water), and doubly distilled water with pH 6.5 were used.

## RESULTS

One of the products formed in samples of treated water and detectable immediately after the irradiation is nitrous acid [5]. The acid was experimentally identified by comparing the absorption spectrum of a sample of the treated liquid with that of nitrous acid formed in the chemical reaction. The results are shown in Fig. 1. Curve 5 is the absorption spectrum of a water sample treated with plasma radiation for 30 min. To obtain nitrous acid, the following reactions were used:

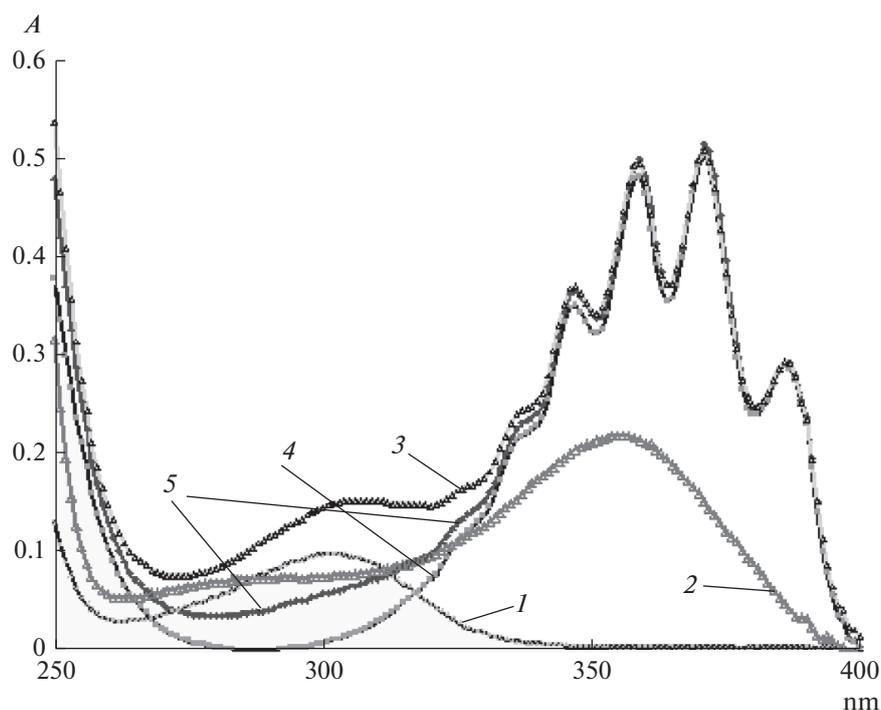


The concentration of  $\text{NaNO}_2$  was 0.69 g/L (0.01 mol/L). The solutions of the acid had pH 2. A weighed sample of  $\text{NaNO}_2$  was added to the acid, and the absorption spectrum was measured immediately after dissolving the powder. The absorption spectra of 0.01 M aqueous  $\text{NaNO}_2$  solution and nitric acid at pH 2 are shown in Fig. 1 by curves 2 and 1, respectively. Sulfuric acid at pH 2 in the wavelength range examined does not make an appreciable contribution to the absorbance. The absorption spectra of the  $\text{NaNO}_2 + \text{H}_2\text{SO}_4$  and  $\text{NaNO}_2 + \text{HNO}_3$  mixtures immediately after their preparation are given by curves 4 and 3, respectively. For both solutions of the mixtures, there is no band due to  $\text{NO}_2^-$  ions, which was detected in the aqueous  $\text{NaNO}_2$  solution. In the  $\text{NaNO}_2 + \text{HNO}_3$  solution, the absorbance at 300 nm attributed to nitric acid (Fig. 1, curve 3) was well below that in the initial nitric acid solution (Fig. 1, curve 1).

The initial pH values of nitric and sulfuric acids were 2. After the addition of  $\text{NaNO}_2$  powder, the pH values were  $2.45 \pm 0.05$  for reaction (1) and  $2.4 \pm 0.05$  for reaction (2). The dissociation constant  $pK_a$  for nitrous acid is 3.4. At the acidity of the medium formed in reactions (1) and (2) (pH 2.4), nitrous acid in the solution is mainly in the form of neutral molecules, so its spectrum can be observed. Nitrous acid is unstable, it decomposes, and four days after the addition of  $\text{NaNO}_2$  powder into the acid, the pH of the acids returns to the pH level of 2.

The coincidence of the absorption lines in the region 330–390 nm for the sample of water after irradiation and for nitrous acid formed in reactions (1) and (2) allows for the conclusion that nitrous acid is the primary product generated by spark discharge plasma. The absorbance values for the liquids studied (water, 0.9% NaCl, and Hanks' solution) after 20 min of treatment with radiation from the IR50 generator are shown in Fig. 2. It can be seen that the absorbance of nitrous acid relative to the baseline is the same for all the three solutions. The spectra of Hanks' solution (curve 3) and 0.9% NaCl (curve 2) samples are indistinguishable. In the physiological saline and Hanks' solution after treatment, there are products that cannot be identified by the spectrum but increase the absorbance over the entire range of 250–400 nm in comparison with the absorption spectra of the treated water (Fig. 2, curve 1). The spectra of the samples 24 h after the treatment are also presented here (curves 4, 5, 6). The spectra of water and 0.9% NaCl are almost indistinguishable (curves 5, 6). A peak at  $\lambda \sim 300$  nm and a special feature at  $\lambda \sim 260$  nm appear in all the samples after 24 hours.

The dependence of the pH of the solutions on the treatment time is shown in Table 1. For pure water and



**Fig. 1.** Identification of nitrous acid.  $A$  is the absorbance of the solutions (D). (1)  $\text{HNO}_3$ , pH 2; (2)  $\text{NaNO}_2$  (0.01 mol/L); (3)  $\text{NaNO}_2 + \text{HNO}_3$ ; (4)  $\text{NaNO}_2 + \text{H}_2\text{SO}_4$  (pH 2); and (5) water; IR50, 30 min.

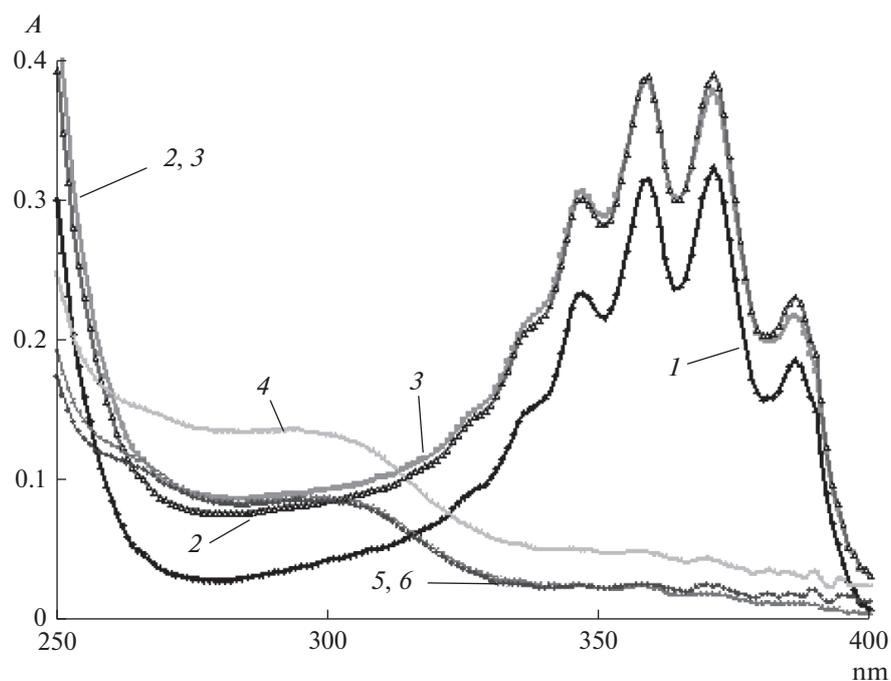
physiological saline, the pH drops rapidly to  $\leq 3.4$ , so that nitrous acid is immediately visible as a group of levels in the range 330–390 nm.

In the Hanks solution, the pH varies more slowly at a short treatment time (up to 4 min); at  $t = 4$  min, pH is 4.36. At this acidity, nitrous acid is present in the solution predominantly in the form of  $\text{NO}_2^-$  ions. This

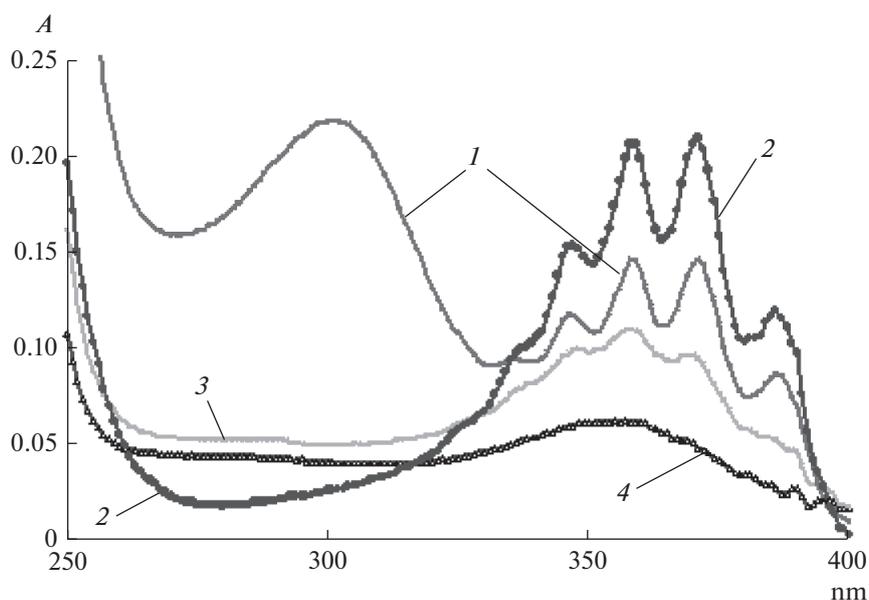
is illustrated in Fig. 3, which depicts the absorption spectra of Hanks' solutions treated for 4 (curve 4, pH 4.36) and 6 min (curve 3, pH 3.62). After 4 min of treatment, nitrous acid can be identified by the peak at  $\sim 360$  nm, curve 4 ( $\text{NO}_2^-$  ions). With increasing treatment time and decreasing pH (curve 3), a structure associated with  $\text{HNO}_2$  molecules appears.

**Table 1.** Acidity of the solutions immediately after the treatment and on the following day. The error of all measurements is  $\pm 0.02$  pH units

Treatment time, min	Immediately after treatment			Next day		
	water	Hanks' solution	0.9% NaCl	water	Hanks' solution	0.9% NaCl
0	6.5	7.3	7.1	6.5	7.3	7.1
1	4.13	6.94	4.29	4.22	7.28	4.72
2	3.66	6.54	3.65	3.73	7.32	3.86
3	3.31	5.96	3.32	3.24	6.60	3.36
4	3.05	4.36	3.13	2.92	4.60	3.06
6	2.89	3.62	2.88	2.66	3.74	2.73
8	2.81	3.32	2.74	2.51	3.26	2.52
10	2.67	3.21	2.67	2.42	3.08	2.44
15	2.49	2.86	2.48	2.27	2.54	2.26
20	2.44	2.65	2.36	2.22	2.36	2.13
25	2.31	2.55	2.28	2.04	2.36	2.03
30	2.31	2.61	2.33	2.05	2.27	2.09



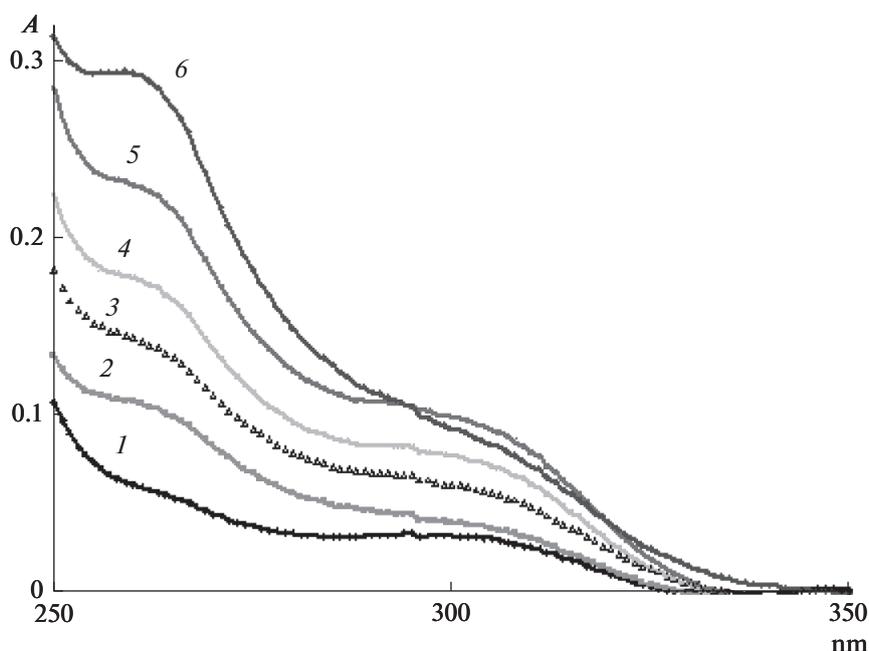
**Fig. 2.** Absorption spectra of samples treated with plasma radiation of the IR50 generator for 20 min ( $A$  is absorbance,  $D$ ), as recorded immediately after the treatment: (1) water, (2) 0.9% NaCl, and (3) Hanks' solution; after 24 h: (4) Hanks' solution, (5) water, and (6) 0.9% NaCl solution.



**Fig. 3.** Absorption spectra of water samples ( $A$  is absorbance,  $D$ ) treated with spark plasma discharge of the IR50 generator: (1) water treatment through quartz glass for 5 h; (2–4) treatment without glass: (2) water, treatment for 10 min, pH 2.67; (3) Hanks' solution, treatment for 6 min, pH 3.62; and (4) Hanks' solution, treatment for 4 min, pH 4.36.

In the case where the discharge cavity is in contact with the liquid being treated, the species formed in the discharge itself will enter into the liquid. To compare the formation of active species under the influence of radiation alone and the combined effect of radiation

and products from the discharge region, a water sample was treated for 5 h through the quartz glass. The spectrum of the sample is shown in Fig. 3, curve 1. For comparison, the spectrum of a sample of water treated for 10 min without the quartz glass (curve 2) is also



**Fig. 4.** Absorption spectra of water samples treated with the IR50 generator for 1 h. The measurements were performed (1) 1, (2) 3, (3) 6, (4) 7, (5) 8, and (6) 13 days after the treatment

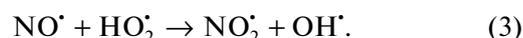
given there. It can be seen that nitrous acid is formed in both cases, but mainly nitric acid is accumulated with the quartz glass for 5 h of the treatment (curve 1, 300 nm peak).

Spectra recorded 1 to 13 days after the treatment of water samples with the IR50 for 1 h are presented in Fig. 4. The next day after the treatment, there are no any traces of nitrous acid in the samples. On the first day, a peak at  $\sim 300$  nm appears, which can be assigned to nitric acid or peroxyxynitrite. The peak increases with storage time, reaches a maximum by the 7th to 8th day and almost disappears on the 13th day (Fig 4, curve 6).

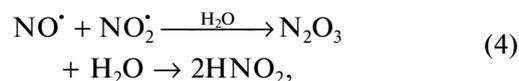
## DISCUSSION

The mechanism of product formation by the action of spark discharge plasma radiation in air was considered in [6]. It was shown that nitric and nitrous acids are produced and the yield of nitric acid is much greater than that of nitrous acid. Those findings agree with the results of this study (Fig. 3, curve 1). At a long duration of the current pulse (150  $\mu$ s), the active species formed during the leading edge (0.1–0.2  $\mu$ s) decayed at their generation sites in the second stage of the discharge when the field strength is low and new species are not produced. As the duration of the current pulse is reduced by a factor of  $\sim 30$  (from 150 to 5–6  $\mu$ s) and the parameters of the front are retained, the probability of the decay of the active species decreases, and they begin to make a significant contribution to the formation of primary products. According to Zeldovich mechanism,  $\text{NO}^\bullet$  radicals are formed in a

spark discharge. Since  $\text{HO}_2^\bullet$  radicals are produced in water by the action of plasma radiation [4],  $\text{NO}^\bullet$  radicals that have entered into the water will be further oxidized:



After this, nitrous acid is formed:



Thus, the primary product formed in water upon its contact with the products formed in the gas phase will be nitrous acid. This conclusion is confirmed by comparing curves 1 and 2 in Fig. 3, which show that after treatment with the plasma radiation alone (curve 1), the absorbance of the nitric acid band (at  $\sim 300$  nm) is almost the same as that of the bands due to nitrous acid (330–390 nm). After the treatment with open discharge, the absorbance of nitrous acid  $A$  is  $\sim 0.22$ , and the nitric band acid is not seen at all (Fig. 3, curve 2).

In addition to nitrous acid, products that are not identifiable by the spectrum and give rise to absorption in the 250–330 nm region are formed in the liquid under irradiation and upon interaction with the discharge products (Fig. 1, curve 5). When only nitrous acid is formed, in particular in reaction (2), the absorbance in this region is much lower, even being zero at wavelengths of 280–330 nm (Fig. 1, curve 4). The for-

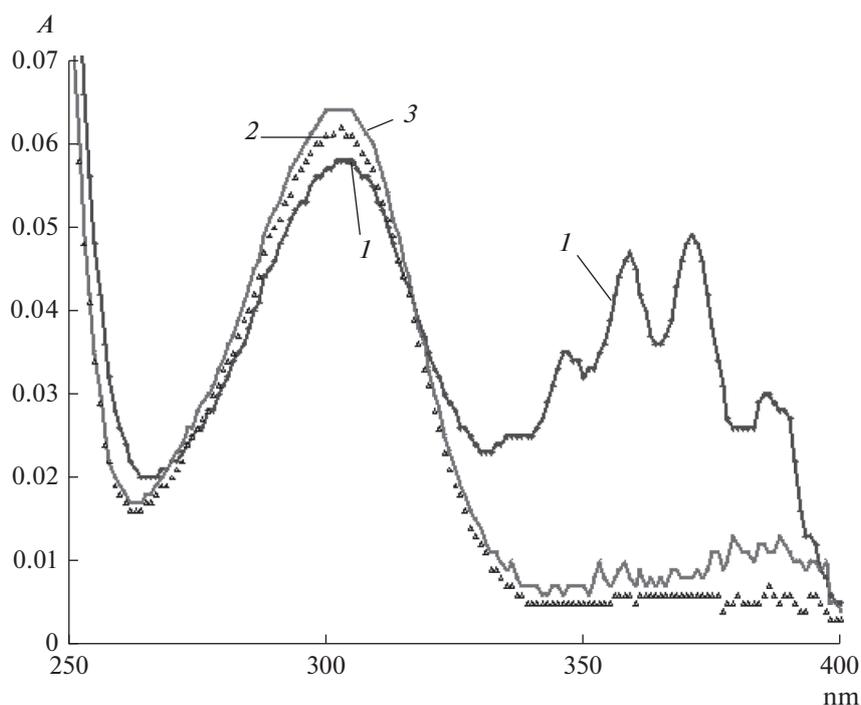


Fig. 5. Spectra of the  $\text{H}_2\text{SO}_4$  solution (pH 2), in which  $\text{NaNO}_2$  powder (0.69 g/L) was added, aged for (1) 2, (2) 6, and (3) 10 days.

mation of species that are not immediately identifiable manifests itself upon their degradation for a long time.

The water samples treated for a 1 h by the IR50 generator were monitored for 13 days. The spectrum of a water sample immediately after the treatment for 30 min is shown in Fig. 1, curve 5, for an hour of the treatment the shape of the spectrum was retained, but the absorbance increased twofold. After 24 h, the peaks of nitrous acid disappeared and a peak at  $\lambda \sim 300$  nm appeared (Fig. 4, curve 1). With an increase in the storage time, the absorbance in the range of 250–330 nm increased. A peak at 260 nm appears and becomes more noticeable over time. The peak at 300 nm increases and reaches a maximum 7 to 8 days after the treatment (Fig. 4, curves 4 and 5). After 13 days, the peak at 300 nm almost disappears, but the absorbance at 260 nm reaches a maximum. The peak at 260 nm can be associated with the dissolution in water of  $\text{N}_2\text{O}_3$  gas, which is the product of decomposition of nitrous and peroxynitrous acids [7, 8]. To test this assumption, containers with samples stored for 8 and 13 days were opened and the absorption spectrum was measured for the next day. The peak at 260 nm in both samples disappeared after that time. Consequently, it is associated with a gaseous product.

In the case when only nitrous acid is formed (reaction (2)), its decomposition occurs in a different way. Figure 5 shows the absorption spectra of the products of reaction (2) for up to 10 days. It should be emphasized that nitrous acid itself decomposes much more slowly in this case. The acid is noticeable in the spec-

trum for the second day (Fig. 5, curve 1), while the peaks of nitrous acid in the spectra of samples of water, physiological saline, and Hanks' solution disappear after 24 h (Fig. 3, curves 4, 5, 6). The peak at 300 nm in reaction (2) slightly increases with an increase in the storage time of the samples (Fig. 5, curves 1–3). This is apparently due to the conversion of residual nitrous acid into nitric acid. The peak at 260 nm in the products of reaction (2) does not appear at all.

In [4], it was suggested that there is the formation of a complex that slowly decomposes to give peroxynitrite as one of its degradation products of its. The peak at  $\sim 300$  nm is mainly associated with peroxynitrite. This assumption is confirmed by the result that the peak at  $\sim 300$  nm disappears during a period of about 13 days (Fig. 4). The peak of nitric acid, formed during the decomposition of nitrous acid, does not vanish during the same time and tends to increase (Fig. 5).

## CONCLUSIONS

Thus, it has been established that with a decrease in the current-pulse duration, the role of active species generated in the discharge itself in the formation of primary products arising in the liquid greatly increases. Nitrosamines are not formed. The main primary product identified by the absorption spectrum is nitrous acid. The yield of nitrous acid under the action of an open source of plasma radiation in water, physiological saline, and Hanks' solution is the same.

The formation of long-lived products in the liquid by the action of spark discharge allows them to penetrate the skin [9] and lead to noticeable changes in biological objects [10–12]. It is assumed that the effect of plasma can selectively cause the death of cancer cells, although the mechanism of this process is not yet clear [13]. Therefore, the radiation of air spark plasma and the products formed in the discharge itself can be used in biomedical research after a detailed analysis of the mechanisms of its effect.

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