Generation of plasma-activated water using a direct piezo-discharge: physicochemical aspects

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Abstract. Recently, interest has grown in plasma-activated media (PAM) and, in particular, plasma-activated water (PAW) in connection with their extensive applications in medicine, pharmacology, agriculture and the food industry. In this paper, we studied the processes of production of reactive oxygen and nitrogen species (RONS) in distilled water under the influence of cold atmospheric plasma (CAP) generated by a source, based on the use of a piezotrans former. The first results obtained in the study of the UV absorbance spectra in distilled water treated with a direct piezo-discharge showed not only the dependence of the RONS production on the exposure time, but also the long lifetime of these RONS in the treated liquid.

1 Introduction

The non-equilibrium non-thermal atmospheric plasma in recent years has attracted researchers in various fields of medicine and biology, since it allows processing liquid media and heat-sensitive materials, such as biological targets, that cannot withstand high temperature and reduced pressure. Such processing methods led to the creation of new technologies that use the so-called cold plasma in medicine, veterinary medicine, the food industry and agriculture (see, for example, reviews [1–4]). To solve the problems associated with these applications, several different methods have been developed for generating a non-equilibrium atmospheric plasma, among which two main directions can be distinguished — the generation of a cold plasma using a flow of gas (or a mixture of gases) to produce a plasma jet and the generation of low-temperature plasma at atmospheric pressure in the air without gas flow. One of the common ways to create a cold atmospheric plasma is the use of a dielectric barrier discharge, in which the discharge current is limited to dozens of microamperes and should not lead to high temperatures of the treated surface. The synergistic effect when exposed to various chemical compounds, energetic electrons and low-energy ions, electromagnetic fields, ultraviolet radiation leads not only to surface modification, but also to changes in the properties of the biological environment being
treated, as well as liquid media, which has found application in medical and biological practice. Numerous works [2, 5–8] proved that CAP can be successfully used for sterilization, wound healing, immunostimulations — this has been used in unique certified plasma medical devices all over the world [9]. Recently, work has been intensified to ascertain the possibility of expanding the plasma medicine to oncological diseases. Of interest is the result of exposure to CAP both directly on the medium with the cells, and on the fluid without cells with the further addition of this fluid to the cell medium or organism. A cascade of chemical reactions involving active particles generated in plasma occurs at the liquid-gas interface, the main effect of which is to enrich the liquid with ROS, such as hydroxyl, peroxyl and superoxide radicals, as well as RNS, such as nitrogen monoxide and peroxynitrite. Plasma activation of liquids (its saturation with RONS) aroused interest in pharmacology. In the past few years, a new line of research has emerged — plasma pharmacy, the results of which will later be used to create new drugs. Studies [7, 8, 10] show that plasma-treated liquids can maintain bactericidal properties for a long time. To describe the processes that occur when a cold plasma acts on various objects and liquids, it is necessary to understand well what chemicals and in what proportions they actually form in the medium itself, how the treatment mode affects the efficiency of the result.

2 Experimental technique

In this work, laboratory prototypes created at the General Physics Institute of the Russian Academy of Sciences were used as sources of CAP. These devices were developed on the basis of piezoceramic transformers [11] and can create both CAP using an inert helium or argon gas flow and a direct piezo-discharge plasma in the atmosphere. The distance to the object can vary in the first case from 1 to 15 mm, and in the second from 0.5 to 3 mm. In this paper, the object of study was both a direct piezo-discharge and PAW.

The operating mode of the piezotransformer allows you to change the excitation voltage of the discharge from 2 kV to 4 kV, at a resonant frequency of about 20 kHz. The voltage and current plots for a direct piezo-discharge and a photograph of the discharge itself are shown in Fig. 1. The duration of discharges that occur when exposed to the medium (distilled water) is 10–20 ns. The total power consumption of the CAP generator, with which the experiments were conducted, did not exceed 6 watts.

![Fig. 1. a) Plots of voltage and current, b) photo of the discharge.](image-url)
Fig. 2. Emission spectrum measurements setup.

The treatment of liquid media was carried out using standard six-well plates, which allow direct plasma treatment of 5 ml of liquid in each well with a change in exposure time from 30 s to 10 min. A direct piezo-discharge is a set of streamers constantly changing their position on the surface of the treated fluid, and the operating mode is chosen so that the change in water temperature does not exceed 0.5 degrees per minute.

Figure 2 shows the scheme for measuring the emission spectra of a direct piezo-discharge.

3 Emission spectrum measurement results

Figure 3 shows a typical emission spectrum of a piezo-discharge, obtained using an AvaSpec-3648 spectrometer (371–920 nm). The spectrum consists of various systems of the N₂ bands, the first negative N₂⁺ system, triplets of atomic oxygen O (777.4 nm and 844.6 nm).

Fig. 3. The emission spectrum of a direct piezo-discharge in the atmosphere under normal conditions.

Fig. 4 shows the spectrum of the second positive nitrogen system, by which the rotational and vibrational temperatures of N₂ were evaluated, using an AVS-HR2000 spectrometer (300...393 nm). This spectrometer was calibrated using an AVALIGHT-HAL-CAL halogen light source.
The rotational temperature $N_2$ was calculated from the unresolved rotational structure of the $0\rightarrow0$ band radiation. The values obtained varied in the range of 1200...1600 K. The vibrational temperatures were calculated as the relative intensity of a series of electronic-vibrational bands {0→1, 1→2, 2→3}, and the series {0→2, 1→3, 2→4, 3→5}. For the first series of bands, the vibrational temperature was 2200...2400 K, and for the second — 2900...3300 K.

When treating liquids with low-temperature plasma, long-lived RNS and ROS compounds appear (often the term RONS is used) — NO$_2^–$, NO$_3^–$, O$_2$, H$_2$O$_2$, etc. The generation of these compounds can be estimated from the change in the ultraviolet absorbance spectra (range 190...280 nm) of the treated medium [12]. The nitrite ion NO$_2^–$ and nitrate ion NO$_3^–$ have the highest absorbance.

To obtain information on the RONS generation in distilled water, absorbance spectra were studied at various plasma treatment doses, i.e. depending on the operating time, the source power was kept stable, and the distance to the object was kept constant (1.5mm). In this case, the method of absorption of UV radiation (UV absorption spectroscopy) was used (Fig. 5). A DDS-30 deuterium lamp was used as a source of UV radiation, and an AvaSpec-2048FT-4-RM spectrometer (199...320 nm) was used as a receiver of UV radiation. As already described above, the treatment of distilled water with a volume of 5 ml was carried out in a standard 6-well plate with a hole with a diameter of 35 mm. The treated water was studied in special quartz cuvettes with a thickness of 1 cm, which transmits UV radiation from 190 nm. In order to obtain the UV transmission spectrum of the treated distilled water, we first recorded a reference (normalizing) UV spectrum that passed through a quartz cuvette with untreated distilled water, then the UV spectrum that passed through a quartz cuvette with treated distilled water was divided by a reference spectrum.

![Fig. 5. UV transmission spectrum measurements setup.](image)

In Fig. 6a shown a typical UV transmission spectrum of the distilled water treated with a piezo-discharge (plasma treatment time was 30 seconds). And Fig. 6b represents the decimal logarithm of transmission (absorbance). Characteristic features of the absorbance (Fig. 6b) are a maximum of about 209 nm, a smooth decline of 15–20% from 209 nm to
200 nm and an relative absorbance value of about 20% of the maximum at a wavelength of 230 nm. Such an absorbance curve is very close to the absorbance curve of nitrite ion NO$_2^-$, and the decline in the 200...209 nm region indicates that the NO$_3^-$, H$_2$O$_2$ and O$_2$ molecules do not make a significant contribution to the absorbance, although the extinction coefficient for NO$_3^-$ is about two times higher than that of NO$_2^-$.

Assuming that the nitrite ion is produced in much larger quantities than the nitrate ion, the NO$_2^-$ concentration was calculated from the absorbance curve. In Fig. 7 is a graph of the production of the nitrite ion NO$_2^-$ in distilled water (volume 5 ml), depending on the exposure time of the piezo discharge.

Fig. 8a shows how the absorbance curve of distilled water changes over time after treatment for 3 minutes. The peak absorbance increases and shifts towards shorter wavelengths, and the region 210...240 nm also shifts. Based on this behavior of absorbance, it can be assumed that with time the nitrite ion partially transforms to the nitrate ion, which has a greater extinction coefficient, and its peak absorbance is 200 nm. Assuming that these changes are small, a quantitative estimation was made of the change in the concentration of the nitrite ion with time after treatment. The evaluation was made based on absorbance at a wavelength of 230 nm, where the nitrite ion has a greater absorbance than the nitrate ion.

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**Fig. 6a.** UV transmittance spectrum of distilled water processed by a piezo-discharge.

**Fig. 6b.** The decimal logarithm of the UV transmission spectrum (absorbance) of distilled water treated with a piezo-discharge. The volume of treated water 5 ml, exposure time 30 seconds.
$y = 46.589x$
$R^2 = 0.998$

**Fig. 7.** The generation of the nitrite ion NO$_2^-$ (in μmol/l) in distilled water with a volume of 5 ml depending on the exposure time of the direct piezo-discharge.

Figure 8b shows the change in the content (concentration) of the nitrite ion NO$_2^-$ in distilled water after treatment with a direct piezo-discharge. Processing was carried out for 3 minutes in the well of the plate with a liquid volume of 5 ml. Changes were tracked for 8 days. The measurements were carried out in two cuvettes, with one cuvette located at room temperature ($T = 23 \, ^\circ C$), and the second cuvette was stored in a refrigerating chamber at a temperature $T = 4 \, ^\circ C$ on the third day. The initial time $t = 0 \, \text{min}$ corresponds to the processing of distilled water.

**Fig. 8a.** Change with time of the absorbance curve of distilled water after treatment. Processing was carried out for 3 minutes in the well of the plate with a liquid volume of 5 ml.
Fig. 8b. The change in the concentration of nitrite ion NO$_2^-$ in distilled water after treatment. Processing was carried out for 3 minutes in the well of the plate with a liquid volume of 5 ml.

From the point of view of the use of activated liquids in biomedical research, agriculture and food preservation, the following parameters of water treated with direct piezo discharges are of great interest: conductivity, redox potential, pH, hydrogen peroxide concentration. Conductivity was measured using a Cond 6+ conductometer (Eutech Instruments), redox potential using an Expert 001-1 multielectrode meter (Econix), pH using an I-500 pH meter (Aquilon). The concentration of hydrogen peroxide was measured using the enhanced chemiluminescence method in the luminol-paraiodophenol-peroxidase system. Details of the measurement technique can be found in the works published earlier [13–15].

4 Conclusions

In this paper, we studied the characteristics of distilled water treated with a direct piezo-discharge. Changes in the processing time of distilled water by direct piezo-discharge in the atmosphere under normal conditions showed that the distilled water is mainly produced with RONS (mainly H$_2$O$_2$ and NO$_2^-$), which can be stored (the concentration changes only slightly) for at least 8 days. Conductivity, redox potential linearly increase depending on the time of treatment of distilled water and slightly vary with time. While the pH decreases depending on the exposure time and also slightly varies with time. Similar experiments are performed on culture media to ascertain possible biomedical applications. The possibility of sufficiently long storage of the treated liquid is shown. This energy-efficient technology can be applied to create plasma-activated media (PAM) of various nature used both in biomedical research, and to improve the quality of planting material and food preservation. The new scientific results obtained as a result of our studies are in good agreement with the data of various scientific studies that have been obtained by other scientists [16–27].

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