Using of direct piezo-discharge in generation of plasma-activated liquid media

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Abstract. This article shows the possibility of plasma-activated liquid media generation using the least energy-consuming source of low-temperature plasma, based on the use of a piezoelectric transformer. The experiments determined the possibility of producing reactive oxygen and nitrogen species in deionized water and culture media. The concentrations of H₂O₂ and NOₓ were estimated depending on the energy deposition.

1. Introduction
Plasma treatment of liquids using cold atmospheric plasma (CAP) has recently attracted much attention due to a wide range of applications, such as water purification, sterilization of surfaces and liquids, increasing seed germination, stimulating plant growth, regenerating wounds, treating socially significant diseases (in particular, oncological) [1–9]. As a rule, for plasma activation of liquids, low-temperature nonequilibrium atmospheric-pressure plasma jets and dielectric barrier discharge (DBD) are used [4, 8–11]. However, both in the case of a plasma jet and DBD, the rate of production of reactive oxygen and nitrogen species (RONS), which play a key role in bactericidal and therapeutic effects, is low [4, 8–14]. In addition, in most cases, plasma is generated using a flow of inert gases (argon, helium), and the cross section of the plasma jet and the region of its interaction with the liquid are limited to several millimeters [3, 6, 13–15]. The low efficiency of RONS production, the need for gas flow and the limited processing volume make this approach to the creation of plasma-activated media (PAM) expensive for use in medicine and agriculture. The most effective and economical method for the production of PAM is the use of high-density low-temperature plasma created by direct discharge in air [2, 12, 16–18]. Studies [19–21] show that plasma-treated liquids can retain bactericidal properties for a sufficiently long time.

To describe the processes that occur when a CAP acts on various objects and liquids, it is necessary to understand well what chemicals and in what proportions are formed in the medium itself, how does the processing conditions affect the effectiveness of the result.

2. Experimental technique
In fig. 1 shows a scheme of an experimental setup for plasma treatment of liquids. It includes a prototype of a source of CAP, created at the GPI RAS. The creation of CAP in this device is carried out using a piezoceramic transformer [22], whereby it is possible to create plasma both in ambient air (direct piezoelectric discharge) and using an inert gas flow of atmospheric pressure (plasma jet). The distance to the processing object can vary in the first case from 0.5 to 3 mm, and in the second from 1 to 15 mm. Deionized water was treated in glass vessels; the liquid volume was 10 ml (Figure 2). Cultural media were treated in six-well plates with a volume of 5 ml in each of the wells (Figure 3). The duration of CAP exposure to liquid media varied from 30 seconds to 10 minutes with an energy deposition of 80
J/min in the case of direct piezoelectric discharge and 40 J/min in the case of a plasma jet. The power consumed by the cold plasma generator did not exceed 10 watts. The objects of study in this work were liquids (deionized water, DMEM culture medium) treated with direct piezoelectric discharge.

![Figure 1. PAM generation setup.](image)

**Figure 1.** PAM generation setup.

**Figure 2.** Deionized water treatment with direct piezo-discharge (a) and with plasma-jet (b)

Chemical reactions that occur in the gas phase and on the surface of a liquid when it is treated with CAP lead to the appearance of long-lived RNS and ROS in the liquid (the generic term RONS is often used) — NO₂⁻, NO₃⁻, H₂O₂, etc. These compounds determine the bactericidal and therapeutic properties of PAM, and their concentration affects the properties of the liquid, such as the redox and pH. In this work, redox was measured using an Expert 001-1 multielectrode meter (Econix), pH using an I-500 pH meter (Aquilon). Hydrogen peroxide concentration was measured using the enhanced chemiluminescence method in the luminol-paraiodophenol-peroxidase system (the measurement procedure can be found in detail in [23–25]). The production of nitrite/nitrate ions NOₓ was evaluated by measuring the ultraviolet absorbance spectra (range 190 ... 280 nm) of the treated medium (the procedure was described in [26]). These measurements were carried out at various doses of plasma treatment, i.e. depending on the operating time, while the power of the source was kept stable, and the distance to the object remained constant.
3. Experimental results

Figure 4 shows the results of redox and pH measurements of plasma-activated water obtained by treating deionized water with a CAP (direct piezoelectric discharge). The power of the plasma source remained unchanged, and the energy deposition varied with an increase in the processing time. The measurements were carried out immediately after treatment and after 24 hours. The graphs show that redox increases linearly with increasing exposure time, and the pH decreases to a value of 3.7. Both of these parameters change slightly after 24 hours, which may indicate that the concentration of long-lived RONS is almost unchanged.

Hydrogen peroxide H₂O₂, formed in PAM, is involved in damage to the cell membrane of microbe and in the weakening of resistance, so it is important to evaluate its concentration. The H₂O₂ concentration increases according to a law close to linear in the processing time interval from 30 seconds to 3 minutes (Figure 5).

![Figure 4](image)

**Figure 4.** Dependence of redox potential (a) and pH (b) on the exposure time. Measurements were taken immediately after processing and after 24 hours.
Figure 5. Dependence of $\text{H}_2\text{O}_2$ concentration in PAW on the exposure time immediately after processing.

\[ y = 11.933x \]
\[ R^2 = 0.9201 \]

Figure 6. Dependence of NO$_x$ concentration in PAW on the exposure time immediately after processing.

\[ y = 31.996x \]
\[ R^2 = 0.9407 \]

Figure 7. Dependence of NO$_x$ concentration in culture medium (DMEM) on the exposure time immediately after processing.
Other RONS that play a significant role in the bactericidal properties of PAM are NO$_2^-$ and NO$_3^-$. The accumulation of nitrite/nitrate ions NO$_x$ was estimated by measuring the absorbance spectra of UV radiation in the treated liquid [26]. An increase in the concentration of NOx depending on the processing time (from 1 to 10 minutes) of deionized water (Fig. 6) can be approximated with high accuracy by a linear function. A similar dependence of the NO$_x$ accumulation is observed when processing the DMEM culture medium, however, the rate of increase in function is several times higher. This is due to the more complex chemical composition of the culture medium, and as a result, a large number of reactions taking place on the surface of the object and inside it.

The concentration of RONS (H$_2$O$_2$, NO$_x$) in a plasma-activated liquid is determined by the total processing time (total energy deposition), so the result was not sensitive to interruptions (up to 5 minutes) during the processing of the medium.

4. Conclusion

In this paper, we studied the characteristics of deionized water and the DMEM culture medium after treatment with CAP generated by a direct piezoelectric discharge in ambient air. The higher energy deposition of direct piezoelectric discharge when exposed to a liquid medium compared with a plasma jet, and as a result, faster RONS production, allows us to consider this method of PAM generation as more efficient and economical.

Redox of plasma-activated deionized water increases linearly with increasing processing time and varies slightly over time. The pH decreases with increasing energy deposition, which correlates with the production of NO$_x$. Concentrations of hydrogen peroxide and nitrite/nitrate ions increase linearly with increasing energy deposition into the liquid medium.

Plasma-activated culture medium was used in experiments on effects on cell cultures. The first results showed the effectiveness of exposure to cancer cells of various types and the differentiated cytotoxicity of plasma-activated media created by direct piezoelectric discharge. Such an energy-efficient technology can find application both in biomedical applications and in agriculture.

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