Proc. Schl. Eng. Tokai Univ., Ser. E
40 (2015) 1-6

# High Performance Liquid Chromatography Analysis of Distilled Water Irradiated with Atmospheric-Pressure Plasma Jet

by

Hiroshi KUWAHATA [*1] and Ikko MIKAMI [*2]

(Received on Mar. 23, 2015 and accepted on May 14, 2015)

**Abstract**

High performance liquid chromatography (HPLC) analysis was performed for distilled water irradiated with an atmospheric-pressure argon (Ar) plasma jet. Three peaks were observed in the chromatogram of the distilled water irradiated with the plasma jet. These peaks corresponded to hydrogen peroxide ($H_2O_2$), nitrate ions ($NO_3^-$), and nitrite ions ($NO_2^-$). Therefore, we found that $H_2O_2$, nitric acid ($HNO_3$), and nitrous acid ($HNO_2$) were generated in distilled water irradiated with an Ar plasma jet. After 30 min of irradiation, the $H_2O_2$, $NO_3^-$, and $NO_2^-$ concentrations were 84.0, 59.8, and 4.0 mg/L, respectively. The $H_2O_2$ and $NO_3^-$ concentrations in distilled water increased proportionally with the plasma irradiation time, whereas the $NO_2^-$ concentration was almost unchanged. We conclude that the $H_2O_2$, $NO_3^-$, and $NO_2^-$ concentrations can be simultaneously determined by HPLC, thus confirming its effectiveness.

***Keywords:*** HPLC, Atmospheric-pressure plasma, Distilled water, Hydrogen peroxide, Nitrate ion

## 1. Introduction

The decomposition of harmful organic compounds in wastewater using on-water discharges and plasmas is a popular area of research. For example, researchers have reported the decomposition of phenol [1-3], organic dyes such as indigo carmine [4, 5], and acetic acid [6] as model persistent organic substances using on-water pulse discharge, as well as the decomposition of methylene blue dye [7, 8] using on-water atmospheric-pressure plasma.

Previously, we reported the decomposition of methylene blue in an aqueous solution using an atmospheric-pressure argon (Ar) plasma jet [9]. In that study, we carried out measurements by absorption spectroscopy and capillary electrophoresis and found that (1) nitric acid ($HNO_3$) was generated in distilled water irradiated with an Ar plasma jet, (2) the generated nitrate ion ($NO_3^-$) contributed to a peak at a wavelength of approximately 200 nm in the absorbance spectrum, and (3) the $NO_3^-$ concentration increased with the plasma irradiation time [10]. Moreover, we measured the $NO_3^-$ and nitrite ion ($NO_2^-$) concentrations by semiquantitative determination using $NO_3^-$ and $NO_2^-$ test strips and flow injection analysis (FIA) based on absorption spectrophotometry using a Cu-Cd reduction column and naphthylethylenediamine. We found that nitrous acid ($HNO_2$), in addition to $HNO_3$, was generated in distilled water irradiated with a plasma jet and that the $NO_3^-$ concentration increased proportionally with the plasma irradiation time, whereas the $NO_2^-$ concentration was almost unchanged [11]. We also reported that hydrogen peroxide ($H_2O_2$) was generated in distilled water irradiated with an Ar plasma jet and that the $H_2O_2$ concentration in distilled water increased with plasma irradiation time, as determined by semiquantitative determination using $H_2O_2$ test strips and by FIA with fluorescence detection [12]. As explained above, the detection method for $H_2O_2$ was different from that for $NO_3^-$ and $NO_2^-$, and their concentrations were individually determined.

In this study, we report that $H_2O_2$, $NO_3^-$, and $NO_2^-$ in distilled water irradiated with an atmospheric-pressure Ar plasma jet can be simultaneously detected by high performance liquid chromatography (HPLC). In addition, we quantify their concentrations by developing calibration curves and show the dependence of each concentration on the plasma irradiation time.

*1 Junior Associate Professor, Department of Electrical and Electronic Engineering
*2 Associate Professor, Department of Chemistry

## 2. Experimental

Figure 1 shows a schematic of the experimental setup used in this study. A copper tube (inner diameter, 4 mm; outer diameter, 6 mm), used as a discharge electrode, is inserted into a dielectric quartz tube (length, 50 mm; inner diameter, 6 mm; outer diameter, 8 mm), around which copper foil (thickness, 0.05 mm; width, 10 mm) is wrapped as a grounding electrode [13]. When a high AC voltage is applied, a dielectric barrier discharge is induced in the quartz tube between these electrodes, and the inflowing argon gas is excited to form a plasma that is then released into the atmosphere.

A plasma jet was generated at an Ar gas flow rate of 10 L/min using a high-voltage power source (LHV-10AC, Logy Electric Co., Ltd.) with a frequency of 10 kHz and an applied voltage of 10 kV. Under these conditions, the plasma jet extended approximately 30 mm from the end of the quartz tube and its maximum diameter was approximately 6 mm [14]. Ten milliliters of distilled water (Wako Pure Chemical Industries, Ltd.) in a 60-mm-diameter glass Petri dish was directly irradiated with an atmospheric-pressure Ar plasma jet for 1－30 min. The distance between the end of the quartz tube and the surface of the distilled water was approximately 15 mm.

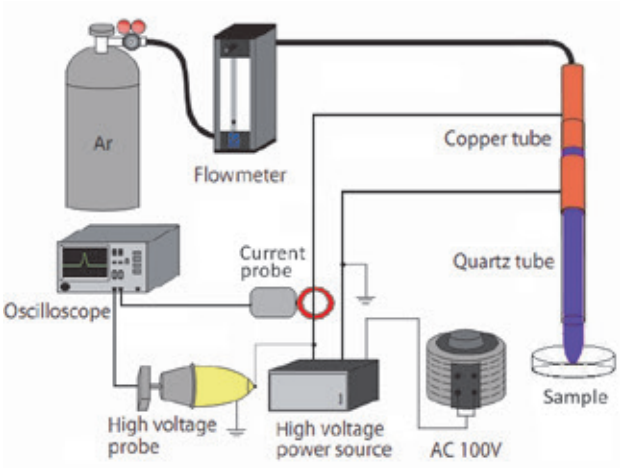


Fig. 1 Schematic of experimental setup.

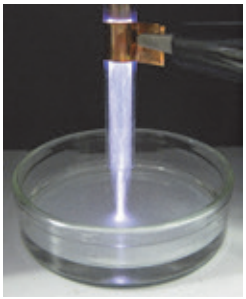

Fig. 2 Plasma jet irradiated onto distilled water.

For the HPLC analysis, a HPLC pump (PU-2080 Plus, JASCO Corporation), a UV detector (UV-2075 Plus, JASCO Corporation), and a column (Hydrosphere C18, YMC Co., Ltd.) were used. The mobile phase was 0.05% phosphoric acid aqueous solution and its flow rate was 1.0 mL/min. The wavelength of UV light at the detection unit was 210 nm. The volume of the sample solution used for the measurement was 20 μL.

## 3. Results

Figure 2 shows a plasma jet irradiated onto distilled water. Streamer discharges are generated in the plasma jet and appear to reach the surface of the distilled water. These

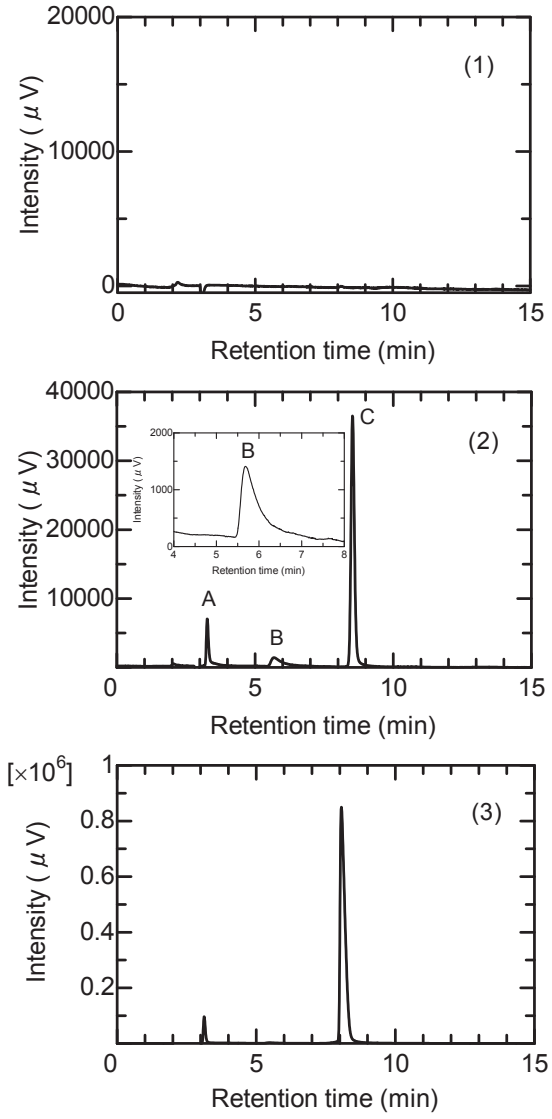


Fig. 3 Chromatograms of distilled water irradiated with plasma jet: (1) before irradiation, (2) after 1 min of irradiation (inset, magnified view of peak B), and (3) after 30 min of irradiation.

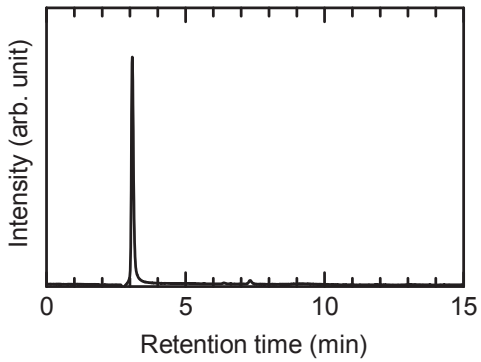


Fig. 4 Chromatogram of $H_2O_2$ aqueous solution.

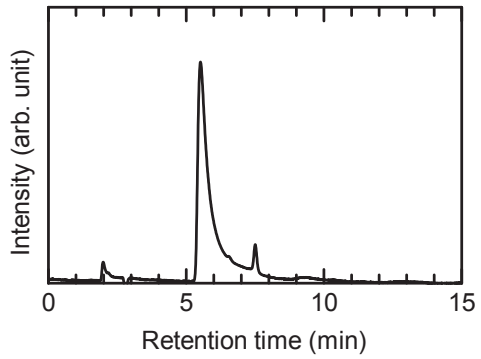


Fig. 5 Chromatogram of $NaNO_2$ aqueous solution.

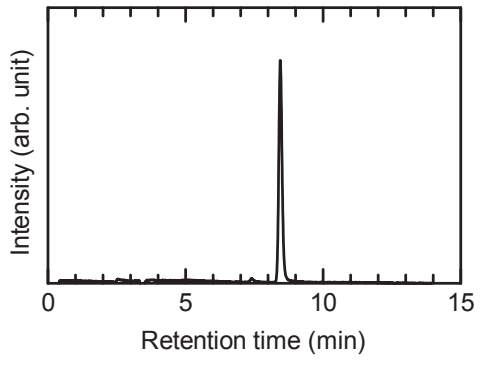


Fig. 6 Chromatogram of $NaNO_3$ aqueous solution.

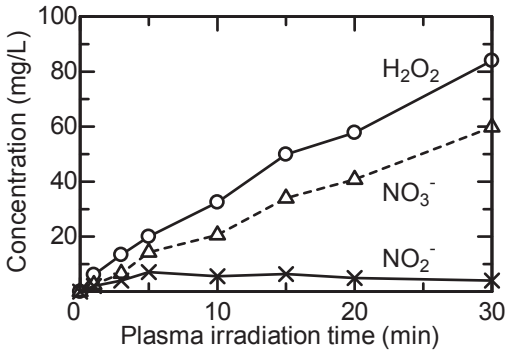


Fig. 7 Dependences of $H_2O_2$, $NO_3^-$, and $NO_2^-$ concentrations in distilled water on plasma irradiation time.

streamer discharges may be flows of electrons. In that case, the electrons in the plasma are considered to reach the surface of the distilled water.

Figure 3 shows chromatograms of distilled water irradiated with a plasma jet. No peak was observed for the distilled water before plasma jet irradiation in Fig. 3-(1). For the distilled water irradiated with a plasma jet for 1 min in Fig. 3-(2), peaks were observed at 3.3, 5.5, and 8.5 min, and are denoted as A, B, and C, respectively. These results indicate that three different substances were generated in the distilled water upon plasma jet irradiation. For the distilled water irradiated with a plasma jet for 30 min in Fig. 3-(3), no peaks other than the above three were observed, but the intensities of the three peaks were increased.

Our previous studies showed that $H_2O_2$, $NO_3^-$, and $NO_2^-$ are present in distilled water irradiated with a plasma jet [10-12]. In this study, a $H_2O_2$ aqueous solution was first analyzed by HPLC. Figure 4 shows a chromatogram of the $H_2O_2$ aqueous solution. A peak corresponding to $H_2O_2$ was observed at 3.3 min, which is in agreement with peak A in Fig. 3-(2). Therefore, peak A was identified to be that of $H_2O_2$.

Next, sodium nitrite ($NaNO_2$) aqueous solution, which contained $NO_2^-$, was analyzed by HPLC. Figure 5 shows a chromatogram of the $NaNO_2$ aqueous solution. A peak was observed at 5.5 min, which is in agreement with peak B in Fig. 3-(2) in terms of both position and shape. Therefore, peak B was identified to be that of $NO_2^-$.

Finally, sodium nitrate ($NaNO_3$) aqueous solution, which contained $NO_3^-$, was analyzed by HPLC. Figure 6 shows a chromatogram of the $NaNO_3$ aqueous solution. A peak was observed at 8.5 min, which is in agreement with peak C in Fig. 3-(2). Therefore, peak C was identified to be that of $NO_3^-$. Thus, HPLC was successfully used to simultaneously detect $H_2O_2$, $NO_3^-$, and $NO_2^-$ generated in distilled water by plasma jet irradiation.

Figure 7 shows the dependences of the $H_2O_2$, $NO_3^-$, and $NO_2^-$ concentrations in distilled water on the plasma irradiation time. Each concentration was determined from the calibration curves developed for each peak intensity in the HPLC chromatograms. The $H_2O_2$ concentration was 0 mg/L before plasma jet irradiation and increased proportionally with the plasma irradiation time: it was 6.1 mg/L after 1 min of irradiation, 13.4 mg/L after 3 min of irradiation, 20.0 mg/L after 5 min of irradiation, 32.5 mg/L after 10 min of irradiation, 49.9 mg/L after 15 min of irradiation, 57.8 mg/L after 20 min of irradiation, and 84.0 mg/L after 30 min of irradiation. The $NO_3^-$ concentration was 0 mg/L before plasma jet irradiation and increased proportionally with the plasma irradiation time: it was 2.6 mg/L after 1 min of irradiation, 6.6 mg/L after 3 min of

irradiation, 14.3 mg/L after 5 min of irradiation, 20.6 mg/L after 10 min of irradiation, 34.0 mg/L after 15 min of irradiation, 40.8 mg/L after 20 min of irradiation, and 59.8 mg/L after 30 min of irradiation. The $NO_2^-$ concentration was almost unchanged even when the plasma irradiation time increased; it was 0 mg/L before plasma jet irradiation, 2.0 mg/L after 1 min of irradiation, 4.0 mg/L after 3 min of irradiation, 7.1 mg/L after 5 min of irradiation, 5.6 mg/L after 10 min of irradiation, 6.4 mg/L after 15 min of irradiation, 5.0 mg/L after 20 min of irradiation, and 4.0 mg/L after 30 min of irradiation. The reason why the $NO_2^-$ concentration negligibly increased with the plasma irradiation time is considered to be that $NO_2^-$ is converted to $NO_3^-$ through binding to the O in the distilled water. O is generated by the dissociation of $O_2$ dissolved in the distilled water. These results were in good agreement with the results obtained in our previous studies [11, 12].

## 4. Discussion

### 4.1 *Generation of* $NO_3^-$ *and* $NO_2^-$

During atmospheric discharge, the reactions below occur [15-17]. Electrons (e) collide with nitrogen molecules ($N_2$) and oxygen molecules ($O_2$) in air to generate nitrogen (N) and oxygen (O) atoms, respectively. The O atoms react with $O_2$ to generate ozone ($O_3$). Through these reactions, nitrogen oxide ($N_xO_y$) is generated. Dinitrogen pentoxide ($N_2O_5$) and dinitrogen trioxide ($N_2O_3$) react with water molecules ($H_2O$) in air to generate $HNO_3$ and $HNO_2$, respectively. In the following equations, M is called the third body and absorbs the internal energy of the generated molecules to stabilize them and prevent their dissociation.

$e + N_2 \rightarrow 2N + e$ (R1)
$e + O_2 \rightarrow 2O + e$ (R2)
$O + O_2 + M \rightarrow O_3 + M$ (R3)
$N + O_2 \rightarrow NO + O$ (R4)
$NO + O \rightarrow NO_2$ (R5)
$NO + O_3 \rightarrow NO_2 + O_2$ (R6)
$NO_2 + N \rightarrow N_2O + O$ (R7)
$NO_2 + O \rightarrow NO_3$ (R8)
$NO_2 + O_3 \rightarrow NO_3 + O_2$ (R9)
$NO_2 + NO \rightarrow N_2O_3$ (R10)
$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$ (R11)
$N_2O_5 + H_2O \rightarrow 2HNO_3$ (R12)
$N_2O_3 + H_2O \rightarrow 2HNO_2$ (R13)
$HNO_3 \rightarrow H^+ + NO_3^-$ (R14)
$HNO_2 \rightarrow H^+ + NO_2^-$ (R15)

Braun *et al.* experimentally confirmed that $O_3$, $N_2O$, $N_2O_5$, and $HNO_3$ were generated in air by atmospheric discharge [15]. Using a gas detector, Miyazaki *et al*. found that $O_3$, NO, and $NO_2$ were generated in a $N_2$-$O_2$ gas mixture upon pulse discharge [18]. Chen *et al*. reported that $O_3$, NO, and $NO_2$ were generated in air by atmospheric dielectric-barrier discharge [19]. They also reported that the $NO_2$ concentration increased with the discharge time, whereas the NO concentration was almost unchanged.

Similar reactions were considered to occur during atmospheric-pressure plasma jet irradiation. In addition to the reactions with $H_2O$ in air, a reaction with $H_2O$ at the surface of distilled water may have occurred in our experiment. Therefore, we considered that $HNO_3$ and $HNO_2$ were generated in distilled water and were ionized to $H^+$ and $NO_3^-$ and to $H^+$ and $NO_2^-$, respectively. As a result, $NO_3^-$ and $NO_2^-$ were considered to be generated in distilled water irradiated with a plasma jet.

Watanabe performed ion chromatography measurements of the concentration of negative ions generated in pure water subjected to a silent discharge [20]. According to their report, $NO_3^-$ was present but little $NO_2^-$ was present in pure water after the discharge. Moreover, the $NO_3^-$ concentration increased linearly with discharge time. He stated that little $NO_2^-$ was present because nitric oxide (NO) and nitrogen dioxide ($NO_2$) generated by discharge rapidly became $HNO_3$. However, the estimated $NO_3^-$ concentrations were not reported. Huang *et al*. performed ion chromatography and reported that $NO_3^-$ was generated in pure water subjected to dielectric-barrier discharge and that the $NO_3^-$ concentration increased with discharge time [8]. They considered that NO and $NO_2$ were generated during dielectric-barrier discharge and that $NO_2$ reacted with $H_2O$ to form $NO_3^-$. However, no estimates of $NO_3^-$ concentrations were reported. Ikawa *et al*. reported that $NO_3^-$ and $NO_2^-$ were generated in distilled water irradiated with an atmospheric-pressure helium (He) plasma jet and that the $NO_3^-$ + $NO_2^-$ concentration increased proportionally with plasma irradiation time, on the basis of the results of ion chromatography [21]. However, they neither determined the $NO_3^-$ and $NO_2^-$ concentrations independently nor stated the reason for the generation of $NO_3^-$ and $NO_2^-$.

### 4.2 *Generation of* $H_2O_2$

The generation mechanism of $H_2O_2$ is considered to be as follows. Electrons (e) [1, 7, 22], metastable excited Ar atoms (Ar*) [23], and metastable excited $N_2$ ($N_2$*) [24, 25] collide with $H_2O$ at the surface of distilled water to generate hydroxyl (OH) radicals and hydrogen (H) atoms in the distilled water.

$e + H_2O \rightarrow OH + H + e$ (R16)
$Ar^* + H_2O \rightarrow OH + H$ (R17)
$N_2^* + H_2O \rightarrow OH + H$ (R18)

The generated OH radicals bond with each other to generate $H_2O_2$ [26-28].

$OH + OH \rightarrow H_2O_2$ (R19)

Miichi reported that 25 mg/L $H_2O_2$ was generated in distilled water subjected to gas-phase creeping discharge for 30 min [4]. Oehmigen *et al*. reported that $H_2O_2$ was generated in distilled water irradiated with on-water atmospheric-pressure plasma and that the $H_2O_2$ concentration increased with the plasma irradiation time to reach approximately 20 mg/L after 30 min of irradiation [29].

## 5. Conclusions

Distilled water irradiated with an atmospheric-pressure Ar plasma jet was analyzed by HPLC.

- In the chromatogram of the distilled water irradiated with an Ar plasma jet, three peaks were observed at 3.3, 5.5, and 8.5 min, which corresponded to $H_2O_2$, $NO_2^-$, and $NO_3^-$, respectively.
- The $H_2O_2$ and $NO_3^-$ concentrations in distilled water increased proportionally with the plasma irradiation time, whereas the $NO_2^-$ concentration was almost unchanged.
- $H_2O_2$, $HNO_3$, and $HNO_2$ were generated in distilled water irradiated with an Ar plasma jet.
- HPLC can be used to simultaneously detect $H_2O_2$, $NO_3^-$, and $NO_2^-$ generated in distilled water by plasma jet irradiation.

## Acknowledgement

The authors are grateful to Professor R. Ohyama of Tokai University for his valuable advice.

## References

1) B. Sun, M. Sato and J. S. Clements: Use of a Pulsed High-Voltage Discharge for Removal of Organic Compounds in Aqueous Solution, J. Phys. D: Appl. Phys., **32** (1999) 1908.
2) W. F. L. M. Hoeben, E. M. Van Veldhuizen, W. R. Rutgers, and G. M. W. Kroesen: Gas Phase Corona Discharges for Oxidation of Phenol in an Aqueous Solution, J. Phys. D: Appl. Phys., **32** (1999) L-133.
3) T. Kuroki, K. Yoshida, H. Watanabe, M. Okubo and T. Yamanoto: Decomposition of Trace Phenol in Solution Using Gas-Liquid Interface Discharge, Jpn. J. Appl. Phys., **45** (2006) 4296.
4) T. Miichi: Decolorization of Indigo Carmine Solution Using Discharge on Surface of a Gas-Layer in Water, IEEJ Trans. Fundam. Mater., **126** (2006) 851. (in Japanese)
5) S. Ikoma, K. Satoh, and H. Itoh: Decomposition of Methylene Blue in an Aqueous Solution Using a Pulsed-discharge Plasma at Atmospheric Pressure, IEEJ Trans. Fundam. Mater., **129** (2009) 237. (in Japanese)
6) T. Miichi, T. Fujimoto and T. Takeda: Decomposition of Persistent Organic Compounds in Water Using Pulsed Discharge on Water, IEEJ Trans. Fundam. Mater., **131** (2011) 853. (in Japanese)
7) K. Kitano, H. Aoki and S. Hamaguchi: Radio-Frequency-Driven Atmospheric-Pressure Plasmas in Contact with Liquid Water, Jpn. J. Appl. Phys., **45** (2006) 8294.
8) F. Huang, L. Chen, H. Wang and Z. Yan: Analysis of the Degradation Mechnism of Methylene Blue by Atmospheric Pressure Dielectric Barrier Discharge Plasma, Chem. Eng. J., **162** (2010) 250.
9) H. Kuwahata, K. Kimura and R. Ohyama: Decolorization of Methylene Blue Aqueous Solution by Atmospheric-Pressure Plasma Jet, e-J. Surf. Sci. Nanotech., **8** (2010) 381.
10) H. Kuwahata, K. Kimura and I. Mikami: Identification of Peak near 200 nm in Absorbance Spectrum of Distilled Water upon Atmospheric-Pressure Plasma Jet Irradiation, e-J. Surf. Sci. Nanotech., **9** (2011) 442.
11) H. Kuwahata and I. Mikami: Generation of Nitric Acid and Nitrous Acid in Distilled Water Irradiated with Atmospheric-Pressure Plasma Jet, e-J. Surf. Sci. Nanotech., **12** (2014) 410.
12) H. Kuwahata and I. Mikami: Generation of $H_2O_2$ in Distilled Water Irradiated with Atmospheric-Pressure Plasma Jet, e-J. Surf. Sci. Nanotech., **11** (2013) 113.
13) R. Ohyama and A. Nagai: Japan Patent (2006) 244938.
14) H. Kuwahata and R. Ohyama: Fundamental Charcteristics of Atmospheric Pressure Argon Plasma Jet and Surface Modification of Glasses, Proc. Sch. Eng. Tokai Univ., Ser. J, **48** (2008) No. 2, 174. (in Japanese)
15) D. Braun, U. Kuchler, and G. Pietsch: Behaviour of $NO_x$ in Air-Fed Ozonizers, Pure Appl. Chem., **60** (1988) 741.
16) S. Mukkavilli, C. K. Lee, K. Varghese, and L. L. Tavlarides: Modeling of the Electrostatic Corona Discharge Reactor, IEEE Trans. Plasma Sci., **16** (1988) 652.
17) J. S. Chang, P. A. Lawless, and T. Yamamoto: Corona Discharge Processes, IEEE Trans. Plasma Sci., **19** (1991) 1152.
18) Y. Miyazaki, K. Satoh, and H. Itoh: Pulsed-Discharge Purification of Water Containing Non-Degrable Hazardous Substances, IEEJ Trans. Fundam. Mater., **128** (2008) 172. (in Japanese)
19) G. Chen, M. Zhou, S. Chen, and W. Chen: The Different Effects of Oxygen and Air DBD Plasma Byproducts on

the Degradation of Methyl Violet 5BN, J. Hazard. Mater., **172** (2009) 786.

20) T. Watanabe: Sterilization by Electrical Discharges and Plasmas, J. Plasma Fusion Res., **75** (1999) 651. (in Japanese).

21) S. Ikawa, K. Kitano, and S. Hamaguchi: Effects of pH on Bacterial Inactivation in Aqueous Solutions due to Low-Temperature Atmospheric Pressure Plasma Application, Plasma Process. Polym., **7**, (2010) 33.

22) M. A. Malik, A. Ghaffar, and S. A. Malik: Water Purification by Electrical Discharges, Plasma Source Sci. Technol., **10** (2001) 82.

23) T. Shirafuji and T. Murakami: Contribution of Electrons, $Ar(^3P_{0,2})$, $H_2O^+$, and $H_3O^+$ to Production of $OH(A^2\Sigma^+)$ in a Micro-Dielectric Barrier Discharge of $Ar/H_2O$, Jpn. J. Appl. Phys., **54** (2015) 01AC03.

24) J. T. Herron: Evaluated Chemical Kinetics Data for Reactions of $N(^2D)$, $N(^2P)$, and $N_2(A^3\Sigma u^+)$ in the Gas Phase, J. Phys. Chem. Ref. Data, **28** (1999) 1453.

25) P. Lukes, M. Clupek, V. Babicky, V. Janda, and P. Sunka: Generation of Ozone by Pulsed Corona Discharge over Water Surface in Hybrid Gas-Liquid Electrical Discharge Reactor, J. Phys. D: Appl. Phys., **38** (2005) 409.

26) M. Sato, T. Ohgiyama, and J. S. Clements: Formation of Chemical Species and their Effects on Microorganisms Using a Pulsed High-Voltage Discharge in Water, IEEE Trans. Ind. Appl., **32** (1996) 106.

27) C. Yamabe, F. Takeshita, T. Miichi, N. Hayashi, and S. Ihara: Water Treatment Using Discharge on the Surface of a Bubble in Water, Plasma Process. Polym., **2** (2005) 246.

28) I. Miyamoto, T. Maehara, H. Miyaoka, S. Onishi, S. Mukasa, H. Toyota, M. Kuramoto, S. Nomura, and A. Kawashima: Effect of the Temperature of Water on the Degradation of Methylene Blue by the Generation of Radio Frequency Plasma in Water, J. Plasma Fusion Res. SERIES, **8** (2009) 627.

29) K. Oehmigen, M. Hahnel, R. Brandenburg, Ch. Wilke, K. –D. Weltmann, and Th. Von Woedtke: The Role of Acidification for Antimicrobial Activity of Atmospheric Pressure Plasma in Liquids, Plasma Process. Polym., **7** (2010) 250.