On the quantification of the dissolved hydroxyl radicals in the plasma-liquid system using the molecular probe method

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ABSTRACT:

Hydroxyl (OH) radical is the most important reactive species produced by the plasma-liquid interactions, and the OH in the liquid phase (dissolved OH radical, OHdis) takes effect in many plasma-based applications due to its high reactivity. Therefore, the quantification of the OHdis in the plasma-liquid system is of great importance, and a molecular probe method usually used for the OHdis detection might be applied. Herein we investigate the validity of using the molecular probe method to estimate the [OHdis] in the plasma-liquid system. Dimethyl sulfoxide is used as the molecular probe to estimate the [OHdis] in an air plasma-liquid system, and the partial OHdis is related to the formed formaldehyde (HCHO) which is the OHdis-induced derivative. The analysis indicates that the true concentration of the OHdis should be estimated from the sum of
three terms: the formed HCHO, the existing OH scavengers, and the OH\textsubscript{dis} generated H\textsubscript{2}O\textsubscript{2}. The results show that the measured [HCHO] needs to be corrected since the HCHO destruction is not negligible in the plasma-liquid system. We conclude from the results and the analysis that the molecular probe method generally underestimates the [OH\textsubscript{dis}] in the plasma-liquid system. If one wants to obtain the true concentration of the OH\textsubscript{dis} in the plasma-liquid system, one needs to know the destruction behavior of the OH\textsubscript{dis}-induced derivatives, the information of the OH scavengers (such as hydrated electron, atomic hydrogen besides the molecular probe), and also the knowledge of the OH\textsubscript{dis} generated H\textsubscript{2}O\textsubscript{2}.

**Keywords:** Hydroxyl radicals; molecular probe; plasma-liquid interactions; dimethyl sulfoxide; formaldehyde

Discharge plasma consists of approximately equal number of energetic ions and electrons, and these plasma species can cause a great number of physical and chemical processes when plasma is in contact with a liquid. By exploiting these processes and their derivative highly reactive species, the plasma-liquid system can find applications in many fields such as water treatment [1-3], plasma medicine [4, 5], nanomaterials synthesis [6-18], and food processing [19-21]. Thereby, it is of great importance to identify and quantify the reactive species in the plasma-liquid interactions, especially for water treatment and plasma medicine in which the treatment efficiency is largely related to the dissolved or transported reactive species. One of the most important reactive species generated by the plasma-liquid interactions is the hydroxyl (OH)
radical. Because of its high reactivity (reduction potential of ~2.8 eV), OH radical has a short lifetime and can only reach a very thin layer of the bulk liquid. However, many applications of the plasma-liquid system are mainly or partially based on the dissolved OH radical-induced processes, such as water treatment and plasma medicine. Thus, it is of great significance to quantify the dissolved OH ($\text{OH}_{\text{dis}}$) radicals generated in the plasma-liquid system.

Previously, the $\text{OH}_{\text{dis}}$ generated from techniques such as Fenton reaction, UV light irradiation of $\text{NO}_3^-$ or $\text{NO}_2^-$ in solution rather than the plasma-liquid system has been quantified by several methods [22]. As OH radicals are highly reactive and have a limited diffusion length in liquid, a direct detection is rather difficult. Therefore, indirect methods have been developed, and one of them is the molecular probe (MP) method. The strategy is to form a long-lived OH-induced derivative by using a molecule to trap or react with OH radicals at first, and then the $\text{OH}_{\text{dis}}$ is indirectly detected by probing the OH-induced derivative. These derivative detection methods can be performed by electron spin resonance (ESR) spectroscopy [23], high performance liquid chromatography (HPLC) [24], and fluoroluminescence (FL) spectroscopy [25]. In order to obtain correct results, it is worth noting that the used MP should react with the OH with a fast speed and the derivatives must be stable under the attack of highly reactive OH radicals.

Several works [26-31] have been reported on applying the MP method to detect the $\text{OH}_{\text{dis}}$ in the plasma-liquid system. However, it is well known that the plasma-liquid system is very complex, and the reactive species generated by the plasma-liquid
interactions consist of not only OH radicals, but also energetic ions, hydrated electrons, and atomic hydrogen etc. In these complicated conditions, there might exist other OH consumed sources, and the OH-induced derivatives might not be as stable as in the sole OH environment. Thereby, we must reconsider the validity of the MP method on the OH detection in the plasma-liquid system.

When the OH radicals produced by the plasma-liquid interactions enter a liquid containing a MP, they will be consumed quickly within a thin liquid layer by a series of parallel reactions mainly with the MP, existing potential OH scavengers (Si), and OH itself to produce related products of PMP, Pi, and H2O2

\[ \text{OH} + MP \rightarrow P_{MP} \quad (1) \]

\[ \text{OH} + \sum_i S_i \rightarrow \sum_i P_i \quad (2) \]

\[ \text{OH} + \text{OH} \rightarrow H_2O_2 \quad (3) \]

The change of OH in solution with respect to time \( (d[\text{OH}] / dt) \) can be expressed by

\[
\frac{d[\text{OH}]}{dt} = G_{OH} - k_{MP}[MP]^a[\text{OH}]^b - \sum_i k_{Si}[S_i]^x [\text{OH}]^y - k_{H2O2}[\text{OH}]^c \quad (4).
\]

where \( G_{OH} \) is the rate of OH radicals dissolved in the liquid, \( k_{MP}, k_{Si}, \) and \( k_{H2O2} \) are the rate constants of OH with MP, the \( i \)th OH scavenger, and OH itself (to form H2O2), respectively. \([MP], [OH], \) and \([Si]\) are the concentrations of MP, OH, the \( i \)th scavenger in liquid, respectively. \( a, b, x, y, c \) are the partial orders of related reactions. In a pseudo steady state \( (d[\text{OH}] / dt=0) \), the \( G_{OH} \) can be expressed as

\[
G_{OH} = k_{MP}[MP]^a[\text{OH}]^b + \sum_i k_{Si}[S_i]^x [\text{OH}]^y + k_{H2O2}[\text{OH}]^c \quad (5).
\]
If the last two terms in Eq. 5 are negligible, and P_{MP} is also stable under the plasma treatment, the total concentration of dissolved OH ([OH_{dis}]) during the plasma-liquid interactions can be obtained by

\[ [OH_{dis}] = \int G_{OH} \, dt = \int k_{MP}[MP]^a[OH]^b \, dt \] (6).

These assumptions are used in most of the cases for detection of the OH_{dis} in the plasma-liquid system [26-31]. But these assumptions might not be valid since there exists various highly reactive species in the plasma-liquid system. In order to verify these assumptions, we design an experiment to inspect the [OH_{dis}] in a plasma-liquid system using the MP method. There exist many MPs for the OH_{dis} detection for the plasma-liquid system, such as 5,5-dimethyl-1-pyrrolineN-oxide [31], disodium salt of terephthalic acid [26, 32], terephthalic acid [27, 33, 34], salicylic acid [35, 36], and dimethyl sulfoxide (DMSO) [26, 32, 37]. To focus our discussion, we choose one of them, DMSO, which is miscible with water. The DMSO can react with OH to form OH-induced derivative, formaldehyde (HCHO).

The experimental setup is illustrated in Fig. 1. The cylinder-like plasma reactor is made from polytetrafluoroethylene (detail parameters of the reactor can be found in Ref. [38]). The plasma treated liquid (200 ml) is circulated by a peristaltic pump with a flow rate of 100 ml/min. The flowing silicone tube is 3 mm and 5 mm in inner and outside diameters, respectively. To generate the atmospheric pressure discharge plasma in open air, a direct current power source (BOHER HV, LAS-20 KV-50 mA, positive polarity) is applied to a solid tungsten steel electrode (4 mm in diameter), and the plasma is generated between the solid electrode and the flowing liquid surface (discharge gap of
3 mm). A graphite rod (5 mm in diameter) is grounded at the bottom of the solution to act as an inert electrode. A 50-kΩ resistor is connected in series with the tungsten steel electrode to avoid the plasma transfer from glow-like discharge to arc. The discharge current (fixed for 30 mA in this study) is achieved from dividing the voltage across a 10-Ω resistor which is in series connected with the graphite electrode. After the plasma treatment, the treated liquid is mixed in a blending beaker by a magnetic stirrer. Oxygen gas (150 sccm, 99.9% in purity) is bubbled into the blending beaker for the oxygen-involved reactions mentioned later. The liquid is an aqueous solution of DMSO or a mixture of DMSO and HCHO.

DMSO (>99.8%), HCHO (37%), and acetic acid (≥99%) were purchased from Xilong Scientific Co., Ltd. Ammonium acetate (≥99%) and acetylacetone (≥99.3%) were purchased from Sinopharm Chemical Reagent Co., Ltd.

Hantzsch reaction [39] was used for the colorimetric estimation of HCHO concentration. We prepared aqueous solutions which contain ammonium acetate (50 g), acetic acid (6 ml), and acetylacetone (0.5 ml) in 100 ml purified water. Samples (1 ml) of the plasma treated liquid were taken from the beaker in a fixed interval, and then they were mixed with 1 ml the prepared solution. The mixed solutions were bathed in heated water (60 °C) for 15 min, and then cooled to room temperature. Absorbances were measured for the mixed solutions in a quartz cell (10 mm in optical thickness) by combining an optical emission spectroscopy (Ocean Optics USB 2000+) and a tungsten halogen light source (Ocean Optics HL-2000). It is well known that the absorbance intensity at 410 nm of the mixed solution is proportional to the HCHO concentration.
The linear relationship between the HCHO concentration and the absorbance intensity at 410 nm was achieved by measuring a series of standard HCHO solutions.

**Figure 1.** Schematic diagram of the experimental setup. Lengths of silicone tubes a, b, c are 20 cm, 20 cm, and 25 cm, respectively. The inner and outside diameters of the tubes are 3 and 5 mm, respectively. Inside the pump, there is a 10 cm-silicone tube (4 and 6 mm in inner and outside diameters) to connect tubes b and c.

DMSO can react with the OH_dis at a very fast rate constant of $6.6 \times 10^9$ M$^{-1}$s$^{-1}$ [40], producing methanesulfinic acid (CH$_3$SOOH), methyl radical (CH$_3$), and at the present of oxygen, HCHO and methanol (CH$_3$OH) via Eqs. 7-9,

\[
(CH_3)_2SO + OH \rightarrow CH_3SOOH + CH_3 \quad (7)
\]

\[
CH_3 + O_2 \rightarrow CH_3OO \quad (8)
\]

\[
2CH_3OO \rightarrow HCHO + CH_3OH + O_2 \quad (9).
\]
The produced methanesulfinic acid [41, 42] or formaldehyde [24, 26] has been taken as the OH\textsubscript{dis}-induced derivative for the OH\textsubscript{dis} detection. The [OH\textsubscript{dis}] is usually considered to stoichiometrically relate to the measured concentrations of methanesulfinic acid (1:1) or formaldehyde (2:1).

In fact, methanol produced by Eq. 9 can react with the OH\textsubscript{dis} at a high rate constant of 9.7×10\textsuperscript{8} M\textsuperscript{-1}s\textsuperscript{-1} [40], and also produce HCHO at the presence of oxygen via Eqs. 10-11 [43],

\[
OH + CH_3OH \xrightarrow{\text{H atom abstraction}} CH_2OH + H_2O \quad (10)
\]

\[
CH_2OH + O_2 \rightarrow O_2CH_2OH \rightarrow HCHO \quad (11).
\]

Therefore, the produced HCHO might come from two pathways by a series of reactions,

\[
2(CH_3)_2SO + 2OH \xrightarrow{\text{a series of reactions}} 2CH_3OO \rightarrow HCHO \quad (12)
\]

\[
(CH_3)_2SO + OH \rightarrow CH_3OH + OH \xrightarrow{\text{a series of reactions}} HCHO \quad (13).
\]

Based on Eqs. 7-9, one can find that two moles of OH\textsubscript{dis} produce one mole of HCHO and two moles of CH\textsubscript{3}OH. If Z (0≤Z≤1) mole of the CH\textsubscript{3}OH produced from two moles of OH\textsubscript{dis} takes part in Reaction 13, we have the following relation: 2+Z moles of OH\textsubscript{dis} radicals correspond to 1+Z moles of HCHO. That is to say, the OH\textsubscript{dis} (used to produce HCHO) concentration is related to the measured concentration of HCHO by a ratio of (2+Z) : (1+Z) rather than 2 : 1.

Based on Eqs. 7-13, the d[HCHO]/dt and d[CH\textsubscript{3}OH]/dt can be expressed as

\[
\frac{d[HCHO]}{dt} = 2k_{DMSO}[DMSO]^{a}[OH]^{b} + k_{CH_3OH}[Z \cdot CH_3OH]^{c}[OH]^{d}
- \sum_{i} k_{HCHO_i}[HCHO]^{e_i}[X_i]^{f_i} \quad (14)
\]
\[
\frac{d[CH_3OH]}{dt} = 2k_{\text{DMSO}}[\text{DMSO}]^a[OH]^b - \sum_i k_{CH_3OH}[CH_3OH]^{gi}[Y_i]^{hi}
\] (15).

where \(X_i\) and \(Y_i\) are the \(i\)th reactants in the liquid able to destruct HCHO and CH\(_3\)OH, respectively. For instance, the OH\(_{\text{dis}}\) can react with HCHO to form formate and the final product carbon dioxide in the presence of O\(_2\) \[44\]. \(e_i, f_i, g_i, h_i\), are the partial orders of related reactions.

In this experiment, only a small ratio of the total DMSO is consumed, [DMSO] can be considered to be constant during the plasma treatment. In addition, for a pseudo steady state (\(d[OH]/dt=0\)), [OH] is a constant. Consequently, \(2K_{\text{DMSO}}[\text{DMSO}]^a[OH]^b\) can be represented by a constant of \(k_1\). We found the third term in Eq. 14 is a constant during the plasma treatment by measuring the [HCHO] variation as shown later in Fig. 3. That means the plasma-induced destruction of HCHO is a pseudo zero-order reaction (reaction rate of \(k_2\)). If we further assume that plasma-induced destruction of CH\(_3\)OH is also a pseudo zero-order reaction (reaction rate of \(k_3\)). Therefore, we have

\[
\frac{d[CH_3OH]}{dt} = k_1 - k_3
\] (16)

\[
[CH_3OH] = (k_1 - k_3)t, \quad ([CH_3OH] = 0 \text{ at } t = 0)
\] (17).

If we assume \(c=d=1\), then

\[
\frac{d[HCHO]}{dt} = k_1 + Z \cdot [(k_1 - k_3)t] - k_2 = Z \cdot (k_1 - k_3)t + (k_1 - k_2)
\] (18)

\[
[HCHO] = Z \cdot (k_1 - k_3)t^2 + (k_1 - k_2)t + C_1
\] (19).

From Eq. 19, the true concentration of OH\(_{\text{dis}}\)-induced HCHO ([HCHO]\(_{\text{true}}\)) should be

\[
[HCHO]_{\text{true}} = [HCHO] + k_2t
\] (20).
Figure 2 presents the measured [HCHO] for the plasma-treated DMSO solutions (10 mM) with different initial [HCHO]. The changes of [HCHO] (Δ[HCHO]) are summarized in Table 1. The temporal [HCHO] can be fitted well by a two-order polynomial as shown in Fig 2. The coefficients of the polynomials are given in Table 2. Therefore, $Z$ in Eq. 19 is not zero. Evidently, $\Delta\text{[HCHO]}$ depends on the initial [HCHO], and its absolute value decreases with increasing [HCHO]. Simply, there must exist the HCHO destruction and the generation of HCHO from CH₃OH during the plasma treatment.

**Figure 2.** Temporal [HCHO] for plasma treatment of aqueous DMSO (10 mM) with different initial concentrations of HCHO. The continuous lines are the data fitted with two-order polynomials, $[\text{HCHO}]=A t^2+B t+C$.

**Table 1.** [HCHO] changes in DMSO solutions (10 mM) after 20-min plasma treatment.

| Initial [HCHO] (µM) | Final [HCHO] (µM) | $\Delta$[HCHO] (µM) |
|---------------------|-------------------|---------------------|
| 720 µM              |                   |                     |
| 450 µM              |                   |                     |
| 300 µM              |                   |                     |
| 150 µM              |                   |                     |
| 0 µM                |                   |                     |
Table 2. Coefficients of the two-order polynomials by fitting [HCHO] with $A_t^2+B_t+C$, and the reaction rate $k_1$ ($2KDMSO[DMSO][OH]$) calculated from $B=k_1-k_2$.

| Initial [HCHO] (µM) | A (µM min$^{-2}$) | B (µM min$^{-1}$) | $k_2$ (µM min$^{-1}$) | $k_1$ (µM min$^{-1}$) |
|---------------------|------------------|------------------|-----------------|----------------|
| 0                   | 0.15             | 4.55             | 0 or 9.78       | 4.55 or 14.33 |
| 150                 | 0.27             | 0.56             | 9.78            | 10.34         |
| 300                 | 0.16             | 0.94             | 9.78            | 10.72         |
| 450                 | 0.35             | -3.21            | 9.78            | 6.57          |
| 720                 | 0.36             | -6.15            | 9.78            | 3.63          |

In order to investigate the HCHO destruction by the plasma-liquid interactions, a HCHO solution with an initial [HCHO] of 628 µM was treated by plasma for 2 h. Figure 3 shows the relationships between the [HCHO] and the plasma treatment time. We can find that the destruction of HCHO by plasma is roughly linear for [HCHO] is higher than 20 µM, and the destruction rate is estimated to be -9.78 µM/min. V.V. Kovačević et al. found that the HCHO with a concentration of 50 µM is stable in water when a dielectric barrier discharge in direct contact with water [37], while in our case, the HCHO is stable under the plasma treatment as [HCHO] ≤ 20 µM. These results imply that plasma-induced destruction of HCHO is a pseudo zero-order reaction, i.e., the third term of Eq. 14 is a constant ($k_2$).
**Figure 3.** Temporal [HCHO] for plasma treated aqueous HCHO solution with an initial [HCHO] of 628 μM.

If we use $k_2=0$ μM/min for the solutions with [HCHO]≤20 μM, and $k_2=9.78$ μM/min for the solutions with [HCHO]>20 μM, we can correct the [HCHO] in Fig. 2 to the [HCHO]$_{true}$ in Fig. 4. The changes of [HCHO]$_{true}$ ($\Delta$[HCHO]$_{true}$) are summarized in Table 3.
**Figure 4.** Temporal concentrations of the HCHO (containing the plasma-destructed HCHO) ([HCHO]true) for plasma treated aqueous DMSO (10 mM) with different initial [HCHO].

**Table 3.** Changes of [HCHO]true in DMSO solutions (10 mM) after 20-min plasma treatment.

| Initial [HCHO] (µM) | Final [HCHO]true (µM) | Δ[HCHO]true (µM) |
|---------------------|----------------------|-----------------|
| 0                   | 344                  | 344             |
| 150                 | 460                  | 310             |
| 300                 | 574                  | 274             |
| 450                 | 735                  | 285             |
| 720                 | 925                  | 205             |

If we only consider the OH\textsubscript{dis} related to the OH\textsubscript{dis}-generated HCHO, we obtain

$$[OH]\textsubscript{HCHO} = \frac{2}{1+Z} [HCHO]_\text{true}$$  \hspace{1cm} (21).

In fact, considering Eq. 5 and the fact of the existence of OH scavengers (S\textsubscript{i}) in the plasma-liquid system, the OH\textsubscript{dis} is consumed not only by forming HCHO, but also by reacting with the existing OH scavengers such as hydrated electrons, atomic hydrogens [40] as well as OH itself, and thus [OH\textsubscript{dis}] in our case can be expressed as

$$[OH\textsubscript{dis}] = \int G_{OH} dt$$

$$= \int \left( k\textsubscript{DMSO}[DMSO]^a[OH]^b + \sum \limits_{i} k\textsubscript{Si}[S\textsubscript{i}]^{x_i}[OH]^{y_i} + k\textsubscript{H2O2}[OH]^c \right) dt$$ \hspace{1cm} (22).

In Eq. 22, besides the first term which can be related to the [HCHO]true, there exist OH\textsubscript{dis} consumed by the OH scavengers such as hydrated electron, atomic hydrogen [40] as well as HCHO (the second term), and the transfer of OH to H\textsubscript{2}O\textsubscript{2} (the third term).
We can calculated the concentration of the HCHO related OH\textsubscript{dis} by Eq. 21, if we know the value of Z. The second term is difficult to be obtained due to the lack of information for the existing OH\textsubscript{dis} scavengers in the plasma-liquid system. Because the H₂O₂ in liquid generated by the plasma-liquid interactions are from two sources: one is from the gaseous OH combination, and the other is from the combination of dissolved OH radicals, we are not able to quantify the [OH\textsubscript{dis}] by measuring the [H₂O₂] in the plasma-treated liquid. Consequently, only the concentration of HCHO related OH\textsubscript{dis} can be estimated by this method if the value of Z is known, and the MP method actually underestimate the concentration of OH\textsubscript{dis} produced by the plasma-liquid interactions.

To summarize, DMSO was used as the molecular probe to estimate the concentration of OH\textsubscript{dis} generated by the plasma-liquid interactions. The results and the analysis imply that the concentration of the OH\textsubscript{dis}-induced derivative, HCHO (used to estimate the [OH\textsubscript{dis}]), needs to be corrected by considering the HCHO destruction and the HCHO production from the OH\textsubscript{dis} produced methanol. From the corrected [HCHO], we can only estimate the concentration of OH\textsubscript{dis} related to the HCHO, while the true [OH\textsubscript{dis}] is in fact difficult to be evaluated due to the ignorance of the information of existing potential OH\textsubscript{dis} scavengers and the knowledge of the OH\textsubscript{dis}-generated H₂O₂. Generally, when using other molecular probes such as terephthalic acid and salicylic acid, one will still encounter the aforementioned difficulties. The estimation of [OH\textsubscript{dis}] by the molecular probe in the plasma-liquid system is usually underestimated due to the complicated reaction environment. One can estimate the [OH\textsubscript{dis}] related to the OH\textsubscript{dis}-induced derivatives (used to probe the OH\textsubscript{dis}), but the concentration of OH\textsubscript{dis}-
induced derivatives might need a correction by considering the destruction of derivatives. Moreover, it is worth noting that the destruction of the OH$_{dis}$-induced derivatives is system dependent since the highly reactive species are system dependent. Thereby, one needs to measure the destruction of the OH$_{dis}$-induced derivatives each time for different plasma-liquid systems.

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[1] Jamroz P, Gręda K, Pohl P and Żyrnicki W 2014 Plasma Chemistry & Plasma Processing 34
[2] Locke B, Sato M, Sunka P, Hoffmann M and Chang J-S 2006 Ind. Eng. Chem. Res. 45 882
[3] Lukes P "Water Treatment by Pulsed Streamer Corona Discharge" Institute of Plasma Physics AS CR: Prague, Czech Republic. Czech Republic: Institute of Plasma Physics 2001.
[4] Fridman G, Friedman G, Gutsol A, Shekhter A B, Vasillets V N and Fridman A 2008 Plasma Processes and Polymers 5 503
[5] Kong M G, Kroesen G, Morfill G, Nosenko T, Shimizu T, Van Dijk J and Zimmermann J 2009 New J. Phys. 11 115012
[6] Saito G and Akiyama T 2015 Journal of Nanomaterials 16 299
[7] Liu J, He B, Chen Q, Liu H, Li J, Xiong Q, Zhang X, Yang S, Yue G and Liu Q H 2016 Electrochimica Acta 222 1677
[8] Kondeti V S K, Gangal U, Yatom S and Bruggeman P J 2017 Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 35 061302
[9] Gupta S K S Plasma Chemistry and Plasma Processing 1
[10] Chen Q, Li J and Li Y 2015 Journal of Physics D: Applied Physics 48 424005
[11] Brettholle M, Höfft O, Klarhöfer L, Mathes S, Maus-Friedrichs W, El Abedin S Z, Krischok S, Janek J and Endres F 2010 Physical Chemistry Chemical Physics 12 1750
[12] Höfft O and Endres F 2011 Physical Chemistry Chemical Physics 13 13472
16

[13] Richmonds C and Sankaran R M 2008 Applied Physics Letters 93 131501
[14] Huang X, Zhong X, Lu Y, Li Y, Rider A, Furman S and Ostrikov K 2013 Nanotechnology 24 095604
[15] Baba K, Kaneko T, Hatakeyama R, Motomiya K and Tohji K 2009 Chemical Communications 46 255
[16] Kaneko T, Baba K, Harada T and Hatakeyama R 2009 Plasma Processes and Polymers 6 713
[17] Shirafuji T, Ueda J, Nakamura A, Cho S-P, Saito N and Takai O 2013 Japanese Journal of Applied Physics 52 126202
[18] Velusamy T, Liguori A, Macias - Montero M, Padmanaban D B, Carolan D, Gherardi M, Colombo V, Maguire P, Srcev K and Mariotti D 2017 Plasma Processes and Polymers
[19] Misra N, Tiwari B, Raghavaraao K and Cullen P 2011 Food Engineering Reviews 3 159
[20] Thirumdas R, Sarangapani C and Annapure U S 2015 Food Biophysics 10 1
[21] Niemira B A 2012 Annual review of food science and technology 3 125
[22] Gligorovski S, Strekowsk S R, Barbati S and Vione D 2015 Chemical reviews 115 13051
[23] Goldstein S, Rosen G M, Russo A and Samuni A 2004 The Journal of Physical Chemistry A 108 6679
[24] Jen J-F, Leu M-F and Yang T C 1998 Journal of chromatography A 796 283
[25] Fang X, Mark G and von Sonntag C 1996 Ultrasonics Sonochemistry 3 57
[26] Sahni M and Locke B R 2006 Industrial & engineering chemistry research 45 5819
[27] Kanazawa S, Furuki T, Nakaji T, Akamine S and Ichiki R "Application of chemical dosimetry to hydroxyl radical measurement during underwater discharge" Journal of Physics: Conference Series: IOP Publishing 2013:012102.
[28] Xiong Q, Liu H, Lu W, Chen Q, Xu L, Wang X, Zhu Q, Zeng X and Yi P 2017 Journal of Physics D: Applied Physics 50 205203
[29] Shiraki D, Ishibashi N and Takeuchi N 2016 IEEE Transactions on Plasma Science 44 3158
[30] Hoeven W, Van Veldhuizen E, Rutgers W and Kroesen G 1999 Journal of physics D: Applied physics 32 L133
[31] Xu H, Chen C, Liu D, Xu D, Liu Z, Wang X and Kong M G 2017 Journal of Physics D: Applied Physics 50 245201
[32] Sahni M and Locke B R 2006 Plasma Processes and Polymers 3 342
[33] Kanazawa S, Furuki T, Nakaji T, Akamine S and Ichiki R 2012 Int. J. Plasma Environ. Sci. Technol. 6 166
[34] Kanazawa S, Kawano H, Watanabe S, Furuki T, Akamine S, Ichiki R, Ohkubo T, Kocik M and Mizeračzyk J 2011 Plasma Sources Science and Technology 20 034010
[35] Yufang G, Xiaobin L and Daiqi Y 2008 Journal of Environmental Sciences 20 1429
[36] Liao X-b, Guo Y-f, He J-h, Ou W-j and Ye D-q 2010 Plasma Chemistry and Plasma Processing 30 841
[37] Kovačević V V, Doj činovič B P, Jovič M, Roglič G M, Obradovič B M and Kuraica M M 2017 Journal of Physics D: Applied Physics 50 155205
[38] He B, Ma Y, Long Z, Li J, Xiong Q, Liu H, Chen Q, Zhang X, Yang S and Liu Q 2017 Journal of Physics D: Applied Physics
[39] Nash T 1953 Biochemical Journal 55 416
[40] Buxton G V, Greenstock C L, Helman W P and Ross A B 1988 Journal of physical and chemical reference data 17 513
[41] Steiner M G and Babbs C F 1990 *Archives of biochemistry and biophysics* 278 478
[42] Jahnke L S 1999 *Analytical biochemistry* 269 273
[43] Zhou X and Mopper K 1990 *Marine chemistry* 30 71
[44] Lukes P, Locke B R and Brisset J L "Aqueous - Phase Chemistry of Electrical Discharge Plasma in Water and in Gas - Liquid Environments" *Plasma Chemistry and Catalysis in Gases and Liquids* 2012:243.