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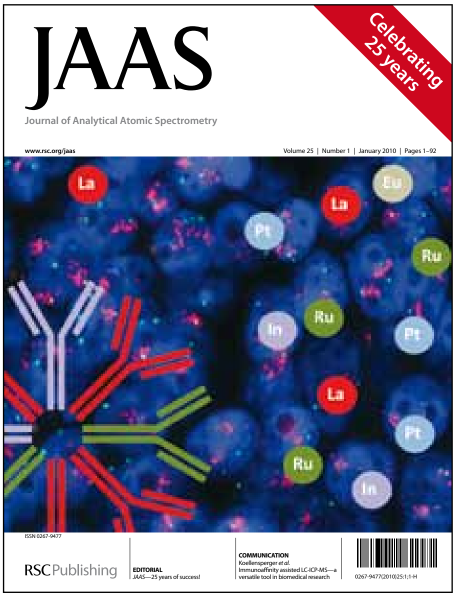

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ARTICLE TYPE

Fundamental properties of a non-destructive atmospheric-pressure plasma jet in argon or helium and its first application as ambient desorption/ionization source for high-resolution mass spectrometry

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Various plasma sources were used as ionization sources for ambient desorption/ionization mass spectrometry (ADI-MS) in the past. In the present study, a plasma jet, termed an atmospheric-pressure damage-free multi-gas plasma jet, which can generate a stable atmospheric low-temperature plasma with various gas species, was investigated and used as an ionization source for ambient MS. First, the OH rotational temperature and electron number density of the plasma were determined spectroscopically. It was found that a relatively low temperature (<350 K) and high-density (10^{14} cm^{-3}) plasma can be generated in helium and argon. Second, the amount of reactive species in the glow-like discharge was indirectly compared to those typically found in a dielectric-barrier discharge jet by means of differences in hydrophilization efficiencies of polyimide films. It was found that the plasma jet was more reactive when the plasma exit was positioned close to the sample (<3 mm). Third, the plasma source was coupled to a high-resolution molecular mass spectrometer (Exactive with Orbitrap mass analyzer) and used for direct solid sample analyses. Commercially available acetaminophen, loratadine, and aspirin tablets were successfully analyzed without any sample pre-treatment. The plasma source was also used for direct solution analysis of model compounds to demonstrate the analytical capacity. Calibration curves were obtained with correlation coefficients of ≧ 0.9975, and limits of detection in the picogram to nanogram range for acetaminophen, loratadine, and aspirin.

1. Introduction

When Teschke *et al.*[1] reported low-temperature plasma jets using dielectric barrier discharges (DBD) in 2005, the development of low-temperature jet-type plasma sources gained significant attention. These plasma sources have now been used for a wide range of applications, including surface modification[2] and biomedicine,[3] because they can be generated using a relatively simple system without the need for vacuum equipment, and exhibit attractive low gas kinetic temperature properties. A wide range of electrode geometries and types of power supplies were used for the low-temperature atmospheric plasma generation. However, many conventional plasma sources had limitations in the number of plasma gas species they can handle (typically, only argon or helium).

To address these limitations, an atmospheric damage-free multi-gas plasma jet was developed by Hirai *et al.* in 2010.[4] This plasma source can generate stable atmospheric plasma jets with various gases, including molecular gas species. This plasma is a kind of glow discharge generated by high-voltage (a few kV) AC power supply (50 Hz to 16 kHz). The plasma gas has a relatively low afterglow temperature, and there is no risk of discharge damage to the target materials. As a result of these characteristics, this plasma source was used in hydrophilization of polyimide films[5] and sterilization of bacteria-covered surfaces[6].

In the field of analytical chemistry, one popular example of an atmospheric-pressure plasma is the corona discharge, which is used as an ionization source of organic compounds for over 30 years.[7] Since the first development of this technique, termed atmospheric pressure chemical ionization (APCI), there has been little progress in the use of plasma sources for molecular mass spectrometry over the years. Recently, however, this situation changed and several plasma-based sources were reported including Direct Analysis In Real Time (DART)[8] and the Flowing Atmospheric Pressure Afterglow (FAPA).[9,10] DART and FAPA are fundamentally different discharges (corona-like vs. glow-discharge-like) and work in different I-V regimes on the Paschen curve. They are considered remote-type plasma sources because the discharge regions are geometrically isolated from the ambient environment. In both cases, high-energy species are generated in the discharge and directed towards to the sample target by the stream of discharge gas, while the discharge itself cannot be perturbed by the sample. The first FAPA study was published in 2008. Around the same time, Harper *et al.*[11] used a remote-type DBD jet (termed low-temperature plasma probe, LTP) as a plasma-based ambient desorption/ionization source

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coupled to molecular mass spectrometry. In DART and FAPA, sample material is typically thermally desorbed by a heated stream of discharge gas emanating from the source and a high-temperature afterglow of the DC glow discharge, respectively. In contrast, Harper *et al*. found that the sample can be desorbed and ionized with a low-temperature LTP probe as well. Desorption efficiency depends on the volatility of the compounds and the matrix, but interesting applications are available[12,13] because of the limited thermal stress that is induced by the LTP source. While the ionization mechanism was recently studied in detail[14,15], the mechanism of sample desorption by LTP is not very well understood at this point.

Plasma-based ambient desorption/ionization mass spectrometry (ADI-MS) using a DBD jet as a probe (*e.g*., LTP), was widely investigated, but few publications reported the use of a truly touchable afterglow from a low kHz frequency glow-like discharge for ADI-MS. Here, atmospheric-pressure damage-free multi-gas plasma jets are considered interesting because they feature high-density plasmas while maintaining a relatively low afterglow temperature. Further, the outer wall of the device published in ref. 5 can be completely grounded for electric shock protection.

In the present study, fundamental plasma properties such as the rotational temperature and electron number density of the atmospheric damage-free multi-gas plasma jet (published in ref. 5) were investigated spectroscopically for the first time. Here, helium and argon were used as plasma gas, respectively, because these gases are often used in ionization sources for ADI-MS. Next, the DBD jet and the atmospheric damage-free multi-gas plasma jet were compared based on the efficiencies of hydrophilization. In doing so, differences in tendencies to generate high-energy species were evaluated indirectly. Finally, the atmospheric damage-free multi-gas plasma jet was used in direct solid and solution analyses, respectively, to evaluate its analytical capacity as an ionization source for high-resolution molecular mass spectrometric analysis.

2. Experimental

2.1 Construction and operation of atmospheric damage-free multi-gas plasma jet source

A schematic diagram and detailed description of the atmospheric damage-free multi-gas plasma jet that was used in this study is given in the publication by Takamatsu *et al*.[5] In brief, the device is made of an interior ball-shaped high-voltage bare copper electrode, which is different type of electrode from the plasma source described in Takamatsu *et al*.[5], connected to a power supply operated at 16 kHz and 9 kV (Plasma Concept Tokyo, Inc., Tokyo, Japan) and grounded to a stainless-steel body. The discharge is generated between these electrodes (discharge gap: 1 mm) at atmospheric pressure and the plasma is pushed to the outside by a gas flow through a hole of 1 mm diameter in the device. In this study, helium and argon (99.999%) were used as discharge gases with flow rates between 0.25 and 2.00 L min^{-1}.

2.2 Gas temperature and electron number density measurements

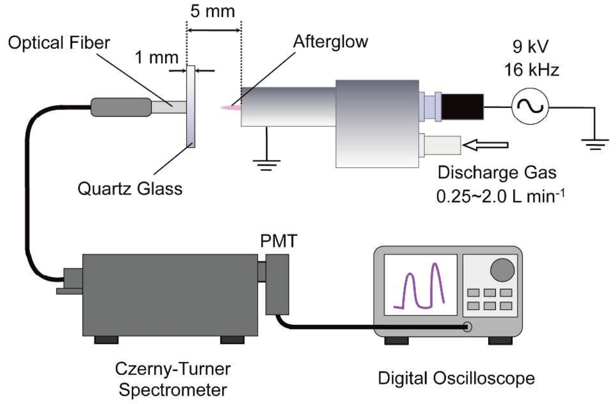

Fig. 1 Schematic diagram of spectroscopic measurement set-up.

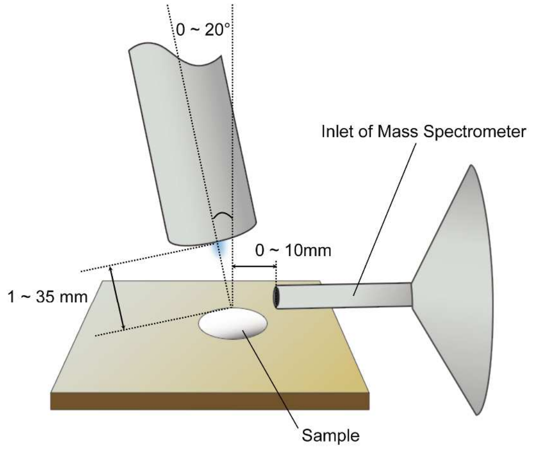

Fig. 2 Schematic diagram of plasma source and sample layout in mass spectroscopic analysis.

To understand the generated plasma, the rotational temperature and electron number density were measured using optical emission based methods. A schematic diagram of the experimental setup is given in Fig. 1. A 500-mm focal length Czerny–Turner monochromator with 1800 grooves/mm grating (Shimadzu Corporation, Kyoto, Japan) equipped with a photo multiplier (R928, Hamamatsu Photonics Company, Hamamatsu, Japan) was used. The entrance slit width was fixed at 40 μm and the spectral resolution of the spectrometer was 46.5 pm FWHM. Emission from the plasma was observed from the axial direction of the plasma jet by an optical fiber placed at a distance of 5 mm from the plasma exit. A thin quartz plate (thickness 1 mm) was placed atop of the fiber to protect it from direct exposure to the discharge. Signals from the monochromator were monitored and recorded using a digital oscilloscope (TDS-680B, Sony/Tektronix Corporation, Tokyo, Japan).

For measuring the gas temperatures in the afterglow region, sheath-type thermocouples composed of SUS316 stainless-steel (length 50 mm and diameter 1 mm) were placed at distances of 1, 5, and 10 mm from the plasma outlet.

2.3 Measurement of surface hydrophilization efficiency

In general, it is thought that a glow-like discharge with bare electrodes tends to generate a greater amount of active species compared to a dielectric barrier discharge, but special experimental instruments are required to measure and evaluate the amounts of reactive species. The latter might be important for planned mass spectrometry applications, especially with regards to ionization and fragmentation. Here, the ability to generate active species was estimated indirectly by studying the performance of both devices in surface hydrophilization (see ref. 5) of polyimide films. . A DBD jet similar to that described by Teschke *et al.*[1] was used as DBD reference source for comparison. Two copper ring electrodes of lengths 7 mm were placed at a distance of 10 mm from one another around a quartz glass tube (o.d. 5 mm and i.d. 3 mm). The distance between the downstream electrode and the edge of the glass tube (*i.e.*, the plasma exit) was 10 mm, and the upstream electrode was grounded. A 16 kHz, 9 kV AC power supply was used for the atmospheric damage-free multi-gas plasma jet and the DBD jet. Polyimide film of thickness 25 µm (TGK 280-18-16-13, Dupont-Toray Corporation, Tokyo, Japan) was used as the sample for surface hydrophilization studies. The polyimide film was moved by a carrier device (GLM20, THK Corporation, Tokyo, Japan) at a rate of 48 mm s^{-1} at a distance of 1 mm from the plasma exit. The degree of hydrophilization was evaluated by measuring the contact angle of water on the surface using a contact goniometer (PG-X, Matsubo Corporation, Tokyo, Japan). Takamatsu *et al.*[5] discussed surface hydrophilization of polyimide films using atmospheric damage-free multi-gas plasma jet in detail.

2.4 Mass spectrometric measurements

After evaluating the fundamental properties of the atmospheric damage-free multi-gas plasma jet, this plasma source was used as the ionization source for ADI-MS. A schematic diagram of the experimental set-up is given in Fig. 2. Helium and argon plasma gas flow rates were kept at 1 L min^{-1}. An Exactive HCD (Thermo Scientific, Bremen, Germany) high-resolution mass spectrometer was used for the measurements. All spectra discussed below were acquired in positive ion mode. To examine direct solid sample analysis capabilities of the device, commercial Paracetamol® tablets (acetaminophen), Claritin® tablets (loratadine 10 mg), and Aspirin® tablets (acetylsalicylic acid 325 mg) were analyzed. Acetaminophen, caffeine, and solvents used for solution analysis were purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). For solution analysis, a sample well plate (5 mm thick glass) with wells of 1 mm depth and 6 mm diameter was used. The sample well plate was heated to 440 K using a nichrome wire. Sample solution (5 µL) was deposited into the well and then probed with the desorption/ionization source. Distance between plasma probe outlet and sample, distance between sample and mass spectrometer interface, and the angle of the plasma jet to the sample well plate, respectively, were adjusted by monitoring analyte signal intensity and the quality of the interface vacuum pressure. Final values were 1 mm, 10 mm, and 0°, respectively, in the case of tablet analysis, and 35 mm, 0 mm from the edge of well, and 20°, respectively, in the case of solution analysis.

3. Results and Discussion

3.1 Measurement of rotational temperatures

Strong emission from the OH rotational band spectrum (due to residual water in the plasma gas and moisture in the ambient air was observed in the atmospheric damage-free multi-gas plasma jet. Rotational temperatures, which are a good approximation of the gas-kinetic temperature, were determined with the Boltzmann plot method using the rotational fine structure of the OH radical at 306.4 nm. Relative intensities of the emission lines at 308.32 nm (excitation energy: 4.0641 eV, A-factor: 701), 308.52 nm (excitation energy: 4.0851 eV, A-factor: 724), and 308.73 nm (excitation energy: 4.1104 eV, A-factor: 736) from the Q_1 branch[16] could be measured, because these lines were free from spectral interferences. After linear regression analysis, correlation coefficients >0.994 were obtained. Rotational temperatures in helium and argon at different plasma gas flow rates in the range of 0.75 to 2 L min^{-1}, which is the range that is expected to be useful for ADI-MS, are shown in Fig.3. Temperatures were measured 5 times per one plot and the error was estimated by calculating standard deviation of 5 times measurement. Although the rotational temperature can be controlled to some degree by changing the plasma gas flow rate, the rotational temperature in the discharge region was much higher than room temperature (>440 K), even when the plasma gas flow rate was set to 2 L min^{-1}. In addition, the gas temperature of the afterglow was measured directly with a thermocouple. The plasma gas flow rate was kept constant at 1 L min^{-1}. The results are shown in Fig. 4. Within the measurement range of 10 mm, it was found that the afterglow region was cooled to some degree by ambient air. Also, the gas temperature in the afterglow that was higher in helium compared to the argon discharge. In plasma-based sources for ADI-MS, plasma gas temperature is strongly related to the desorption efficiency of the sample.[17,18] Thermal desorption is reported to enhance when the gas temperature is above room temperature (375–525 K), but thermal damage to heat-sensitive substrates such as living tissues and increased compound fragmentation might be caveats. Means of afterglow temperature control would allow a temperature-controlled desorption process. For example, Takamatsu *et al.*[5] reported that an almost room-temperature afterglow can be achieved in the device used here when a relatively high gas flow rate of 5 L min^{-1} is applied. Under the present experimental conditions, the plasma was still touchable, but for a short period of time. It is expected that the technique for controlling plasma gas temperature[19] can be used for balancing desorption efficiency and thermal damage according to the sample characteristics in the range of gas flow rates appropriate for MS.

3.2 Measurement of electron number density

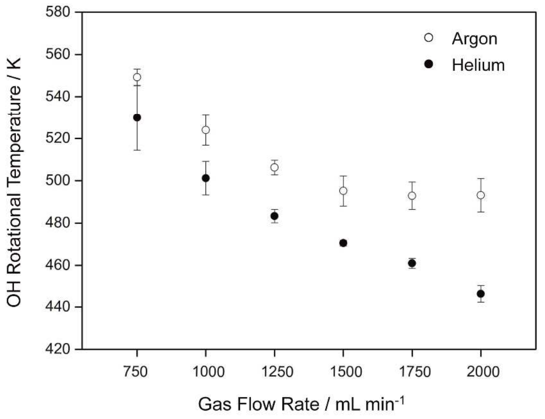

Fig. 3 OH rotational temperatures of helium and argon atmospheric damage-free multi-gas plasma jets at different gas flow rates.

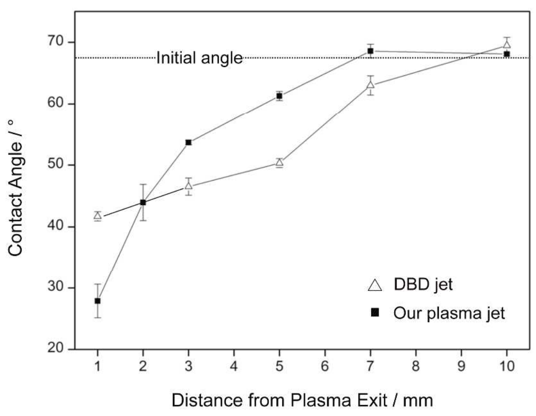

Fig. 5 Hydrophilization efficiency of polyimide film surface *vs.* sample distance from plasma exit using atmospheric damage-free multi-gas plasma jet and DBD jet. Lower contact angle indicates higher efficiency of hydrophilization.

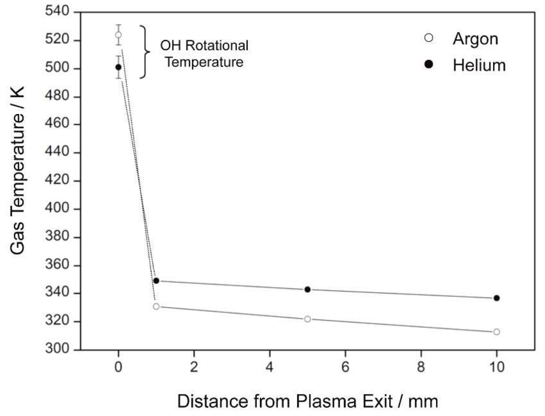

Fig. 4 Gas temperatures in afterglow region measured using thermocouple placed at distances of 1, 5, and 10 mm from the plasma outlet. The plasma gas flow rate was kept constant at 1 L/min.

The electron number density is an important parameter for evaluating plasmas for analytical use because it can be related to the amount of electron impact excitation/ionization in the source. This parameter also provides an indication of the density of important positive ions generated in the plasma such as He^+, He_2^+ and N_2^+.[14] The electron number densities of helium and argon atmospheric damage-free multi-gas plasma jets were measured using the Stark broadening of the hydrogen-beta (H_β) 486.133 nm line, keeping the gas flow rate at 1 L min^{-1}. An instrumental broadening of 46.5 pm (full-width at half-maximum, FWHM) was determined in advance by measuring the Hg I 435.835 nm line from a low-pressure Hg lamp. The measured $H_\beta$line from the plasma was fitted with a Voigt profile including the instrumental function as a Gaussian component. The Lorentzian component width (FWHM) of the $H_\beta$line (He: 94.5 pm, Ar: 135 pm) was then determined. Because the van der Waals broadening is not negligible in atmospheric low-temperature plasmas, van der Waals broadening (FWHM) of the $H_\beta$line (He: 31.2 pm, Ar: 65.4 pm) was estimated by Griem's theory[20] using the rotational temperatures calculated in the previous section. The van der Waals broadening was then subtracted from the Lorentzian component width (FWHM) of the $H_\beta$line, and the Stark broadening of the $H_\beta$line (He: 63.3 pm, Ar: 69.2 pm) was determined. The average electron number density for end-on viewed helium and argon plasma were then estimated from the numerical formula given by Gigosos *et al.*[21] to be 1.7 × 10^{14} cm^{-3} and 2.0 × 10^{14} cm^{-3}, respectively. The electron density of the helium DBD jet, which was used for comparison of the hydrophilization efficiency (see below), was determined in the same way; it was found to be 4.3 × 10^{13} cm^{-3}. Chen *et al.*[14] also measured the electron density near the plasma exit of their DBD jet and the reported value was 9.9 × 10^{12} cm^{-3}. Clearly, the results depend on the type of power supply, applied power, measurement method, and observation position, but a high-density plasma can be generated more easily by a two-electrode glow discharge compared to a conventional DBD jet because electrons are easily supplied to discharge. Electron number densities for the DBD jet studied here were slightly higher than literature values. It was observed that the discharge extended onto the metal part of the optical fiber tip because the plasma has some electrical potential and that the fiber tip is almost grounded. This elongation and strengthening of the discharge is believed to be responsible for the higher electron number density.

3.3 Comparison of reactivities using surface hydrophilization

Because atmospheric damage-free multi-gas plasma jets can generate stable atmospheric low-temperature plasmas with various gases, chemical reactions between the plasma and the sample can be controlled by changing the plasma gas species. However, surface hydrophilization can be achieved at some level even when noble gases such as helium or argon are used as plasma gas. The effect is caused by reactive radicals and ions that are formed through a reaction pathway of high-energy species (*e.g.*, electrons and metastable helium or argon species) and the ambient molecular gas (nitrogen, oxygen, carbon dioxide). In the

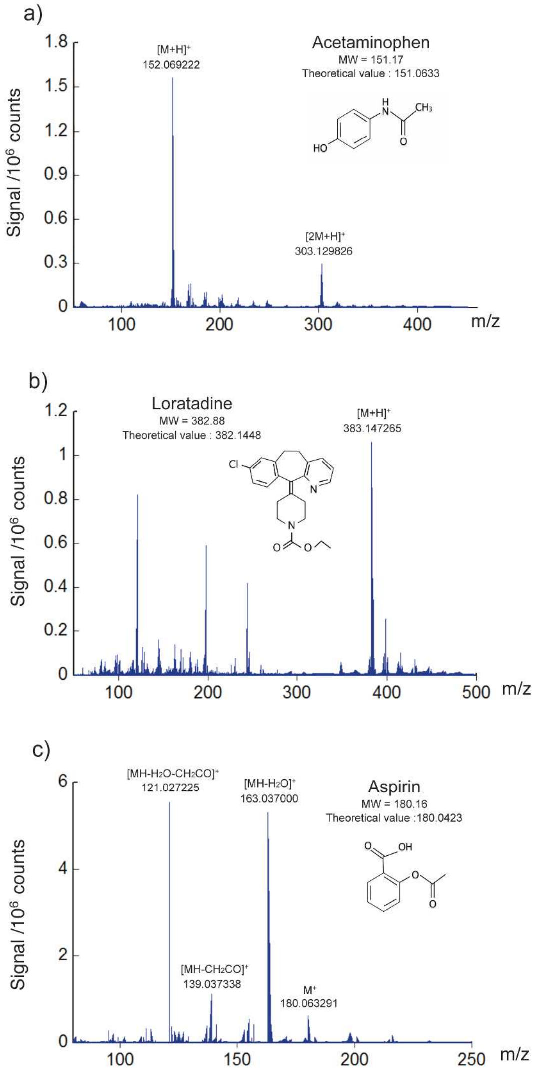

Fig. 6 Typical mass spectra obtained for detection of ingredients in (a) Paracetamol tablet, (b) Claritin® tablet (loratadine 10 mg), and (c) aspirin tablet (acetylsalicylic acid 325 mg) using argon atmospheric damage-free multi-gas plasma jet as desorption/ionization source.

present study, the difference between the amounts of high-energy species generated by the atmospheric damage-free multi-gas plasma and DBD jets, respectively, was determined indirectly from differences in the efficiencies of surface hydrophilization of polyimide film. The contact angle, which is the angle where a drop of water interface meets a surface, was used for the evaluation of the surface hydrophilization because lower contact angle means high hydrophilization efficiencies. Helium was used as the discharge gas. Contact angles were measured 5 times per one plot and the error was estimated by calculating standard deviation of 5 times measurement. As shown in figure 5, the atmospheric damage-free multi-gas plasma jet was more effective for surface hydrophilization when the distance between plasma exit and sample was less than 2 mm. However, the hydrophilization efficiency of our plasma jet decreased drastically with increasing distance, and the efficiency of the DBD jet became superior to that of our plasma jet at a distance of 3 mm. The hydrophilization efficiency of the DBD jet decreased slowly compared to our plasma jet with increasing distance between 1 and 5 mm. The hydrophilization effect could no longer be observed at a distance of 7 mm using our plasma jet, but the DBD jet still could hydrophilize the sample to some extent. This result can be explained by the difference between the types of discharge of these two plasma jets. It is thought that a DBD jet is formed between a high-voltage electrode and a distant outside atmosphere, which can be regarded as the ground potential, along a discharge channel developed by laminar helium gas flow,[22] *i.e.*, a relatively high-density reactive plasma can be formed in the range of distances at which sufficient purity of the helium can be maintained. The hydrophilization effect is therefore maintained at some level if the distance between the plasma exit and the sample is increased. Chen *et al.*[14] reported the spatially resolved optical spectroscopy measurements of reactive species generated from their DBD jet. In their results, emissions from N_2^+ 390.5 nm and O I 777.2 nm can be observed over 10 mm away from the plasma exit under some conditions. However, a discharge channel is not formed between the electrode and a distant ground in an atmospheric damage-free multi-gas plasma jet because the body is grounded. The plasma that is pushed outside by the gas flow is inactivated at a relatively short distance. The hydrophilization effect of our plasma jet therefore decreased rapidly with increasing distance. However, as a result of the high-density electrode discharge, the reactivity of our plasma jet is higher than that of DBD at the short distances that reactive species can reach. Of course, it also depends on other factors, but more reactive conditions can be achieved using an atmospheric damage-free multi-gas plasma jet than with a DBD plasma jet because the high-density and reactive plasma can be close to the sample because of its damage-free characteristics. Moreover, the discharge conditions of the DBD jet easily change, depending on the electric potential of the sample, as mentioned above. In contrast, an atmospheric damage-free multi-gas plasma jet can keep almost the same discharge conditions, regardless of the type of sample.

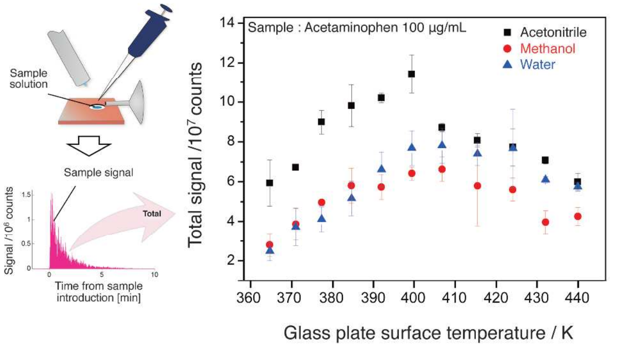

Fig. 7 Relationship between integrated sample signals obtained from 5 µL of acetaminophen (100 µg mL^{-1}) solution and surface temperature of sample well plate under different solvent conditions.

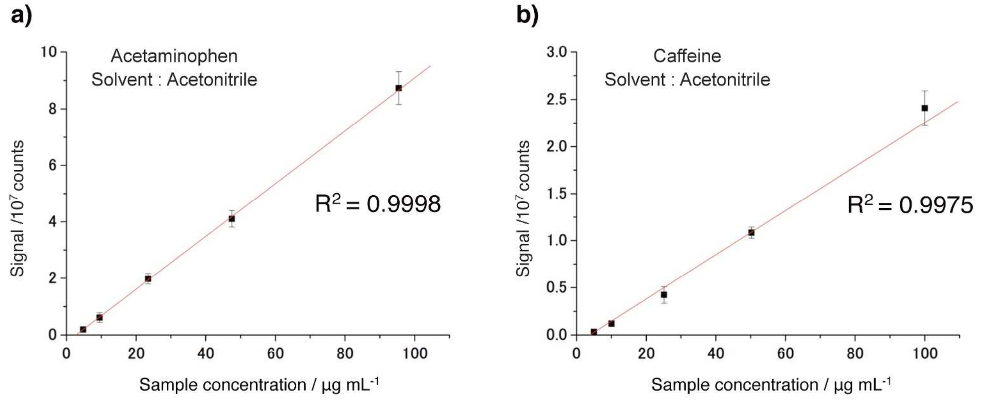

Fig. 8 Plots of signal *vs.* concentration of (a) acetaminophen in acetonitrile and (b) caffeine in acetonitrile, showing the linear relation in the range 1–100 μg mL^{-1}.

3.4 Application to solid sample analysis

Because an atmospheric damage-free multi-gas plasma jet can generate a relatively low-temperature and high-density plasma jet, as described above, it is interesting to apply this plasma source to ADI-MS. Direct solid sample analysis was examined using commercial pharmaceutical tablet samples. Based on the signal intensity and the level of the interface vacuum, argon was used for these experiments. Paracetamol, loratadine, and aspirin tablets were used as samples. The results are shown in Fig. 6. These three samples were therefore analyzed directly using the atmospheric damage-free multi-gas plasma jet. Protonated acetaminophen and its dimer were readily detected at *m*/*z* 152 and 303, respectively, in paracetamol analysis. In loratadine analysis, protonated loratadine was observed at *m*/*z* 383 as the base peak. In aspirin analysis, typical fragments of the sample were detected at *m*/*z* 121 $[MH\text{-}H_2O\text{-}CH_2CO]^+$, 139 $[MH\text{-}CH_2CO]^+$, and 163 $[MH\text{-}H_2O]^+$, and the sample ion was detected at *m*/*z* 180. In the paracetamol and loratadine analyses, the oxidized sample ions, $[M+O+H]^+$, were also detected at signal intensities 10% and 20% those of the base peaks, respectively. In the atmospheric damage-free multi-gas plasma jet, a high-density glow discharge is generated very close to the outside atmosphere. According to the surface hydrophilization results and optical emission measurements in Takamatsu *et al*.,[5] it is thought that ambient air easily diffuses into the discharge region and not only nitrogen molecular ions, which play an important role in sample protonation,[23] but also reactive oxygen radicals are prone to generation. This effect plays a useful role in surface hydrophilization but is unwelcome in ADI-MS applications because the spectrum is complicated by sample oxidation. Because atmospheric plasma reacts intricately with ambient air, the gas atmosphere surrounding the sample should be controlled for detailed research concerning the reaction process.

3.5 Application to solution sample analysis

One of the advantages of a plasma ion source is that the plasma can ionize a gas sample directly. Quantitative analysis of vaporized solution samples was therefore examined using an atmospheric damage-free multi-gas plasma jet. Sample solutions were heated and vaporized using a sample well plate and the plasma was used to ionize the vaporized sample gas. Helium was used for this experiment, considering the signal intensity and the level of the interface vacuum. First, sample heating conditions for were optimized for best sensitivity by analyzing 100 μg mL^{-1} acetaminophen in acetonitrile, methanol, and water, respectively. A sample of 5 μL was analyzed and the extracted ion signal was integrated to get the peak area of the transient mass spectrometric signal of acetaminophen. Then, the relationship between the peak area and the surface temperature of the sample well plate was examined in the range 365–440 K. The results are shown in Fig. 7. Maximum signal intensity was obtained when the surface temperature of the sample well plate was 399–406 K. It was found that the signal intensities differ depending on the solvent, but no correlation with vapor pressure or polarity of the solvent was found. Further investigation is needed to understand this effect. Based on these results, the temperature of the sample well plate was adjusted to 399 K in the case of acetonitrile, and 406 K in the case of methanol and water. Under these conditions, acetaminophen and caffeine (molecular weight 194.19 g/mol) solutions were analyzed in the range 5–100 μg mL^{-1}. The calibration curves of acetaminophen and caffeine in acetonitrile are shown in Fig. 8. In all cases, correlation coefficients were ≧ 0.9975. Limits of detection (LODs) of acetonitrile, methanol, and water solutions of acetaminophen, and acetonitrile solutions of caffeine, were calculated from $S/N = 3$, and the results were 123 pg, 268 pg, 149 pg, and 1.44 ng, respectively. These LODs were inferior to those obtained using LTP-MS (LOD of LTP-MS: subpicograms to picograms).[24] It was not possible to place the plasma source close enough to the sample and the inlet of the mass spectrometer because of the relatively high helium gas flow rate; it is therefore thought that the most reactive afterglow region was not be able to be used for ionization of the sample gas. Reasonable linearity of the calibration curve and sensitivity were obtained under the present conditions but the atmospheric damage-free multi-gas plasma jet needs to be modified for analytical use (*e.g*., using a low plasma gas flow rate) to achieve a better analytical performance.

Conclusion

In the present study, an atmospheric damage-free multi-gas plasma jet, which can generate various stable gas plasmas, was characterized by measuring the rotational temperature and electron density. It was found that the rotational temperature was strongly affected by the gas flow rate, but relatively low-temperature (<350 K) and high-density (10^{14} cm^{-3}) plasmas could be generated with helium and argon. Moreover, by comparing the differences between the hydrophilization abilities for polyimide film of the atmospheric damage-free multi-gas plasma jet and a DBD jet, the differences between the generation behaviors of high-energy species were indirectly evaluated. It was found that our plasma jet was more reactive when the plasma exit was sufficiently close to the sample (<3 mm). The distance dependence of the hydrophilization efficiency of the DBD jet was explained by its discharge characteristics. The atmospheric damage-free multi-gas plasma jet was then coupled with a mass spectrometer and commercial tablet samples (acetaminophen, loratadine, and aspirin) were directly analyzed. In addition, acetaminophen and caffeine solution samples were vaporized and analyzed using our plasma jet under optimal heating conditions. As a result, calibration curves were linearly fitted, with correlation coefficients of ≧0.9975, and LODs were obtained at picogram to nanogram levels. These results show the possibilities of using atmospheric damage-free multi-gas plasma jets as desorption and ionization sources, but further optimization of the plasma source is needed to achieve the same level of performance as that of LTP-MS.

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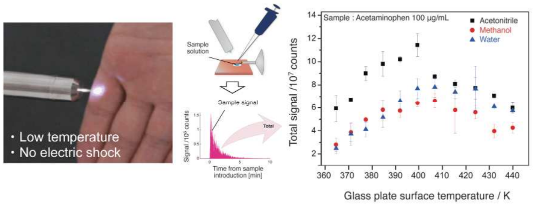

Atmospheric damage-free multi-gas plasma jet, which can generate stable atmospheric low-temperature plasma with various gas species, was investigated and used as an ionization source for ambient MS