

Development of a Remote-from-Plasma Dielectric Barrier Discharge Ion Source and Its Application to Explosives

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The design of a new type of dielectric barrier discharge (DBD) ion source for ambient ionization is described. In this ion source, the DBD plasma is confined in the DBD tube so that the sample gases can be ionized just outside of the discharge tube by DBD excited helium gas without being exposed to the plasma jet. The findings indicate that the ion source is capable of the soft and high-sensitive ionization of explosives.

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1. Introduction

Since its introduction by Horning *et al.*, the direct-current (DC) corona discharge has been routinely used for atmospheric-pressure chemical ionization for the analysis of volatile compounds¹⁾ and the recent successful achievement of DART (direct analysis in real time).²⁾ The DC corona discharge is easily operated and has a reasonable sensitivity for the detection of many types of analytes. However, the corona discharge current is limited to at most $\sim 10\ \mu\text{A}$ and the plasma densities attainable are in the range of $10^9\text{--}10^{13}\ \text{cm}^{-3}$. In contrast, dielectric barrier discharge (DBD) is capable of generating a plasma with plasma densities that are two to three orders of magnitude higher than the DC corona discharge, *i.e.*, $10^{12}\text{--}10^{15}\ \text{cm}^{-3}$.³⁾ To exploit this advantage, a DBD ion source was recently developed by Zhang *et al.* in 2007.^{4), 5)} Due to its high plasma density, abundant ionizing reagents (*e.g.*, electronically excited metastable species, positive and negative reagent ions, and electrons) should be generated by the DBD ion source.³⁾ The study by Zhang *et al.*, published in 2007, triggered the application of the DBD discharge to mass spectrometry.^{6), 7)} In these recent studies, the sample surfaces were exposed to the DBD plasma jet for the desorption/ionization of analyte molecules on the sample surfaces. The main aim for exposing the sample surface to the plasma jet is to promote the desorption of the analyte molecules from the surface, followed by the ionization of the desorbed molecules by the barrier discharge plasma.

We were also investigating the applications of DBD to mass spectrometry at about the same time that

Zhang's pioneering work appeared.^{4), 5)} At that time, the main objective of our research was focused on the detection of explosive materials such as DNT (dinitrotoluene), TNT (trinitrotoluene), TATP (triacetone triperoxide), HMTD (hexamethylene triperoxide diamine), *etc.* for a governmental security/safety project.⁸⁾

In our preliminary experiments, we initially attempted to desorb/ionize the explosive samples by exposing them to the DBD plasma jet. The results showed that fragment ions, as well as ions whose m/z values were higher than the molecular weights of the analytes were produced, in addition to protonated molecules and/or molecular ions. The formation of higher-mass ions was a serious problem in our research project, because it tended to give the false-positive ion signals in cases of safety/security applications.⁸⁾ It was found that the relative abundances of fragment ions and higher-mass ions to those of the protonated molecules and/or molecular ions decreased drastically when the distance between the plasma and the sample was increased. Therefore, fragment ions and higher-mass ions must be mainly originated from some complex chemical reactions that occur in the DBD plasma, in which energetic electrons are likely to play a major role. Because of this drawback, we concluded that exposing the sample to the plasma jet was not an appropriate procedure to follow. After some trial and error, we have developed a new DBD ion source for the detection of explosives that has the capability of both high-sensitive and soft ionization. This ion source was found to be versatile and can be used for the ambient detection of not only explosives but also a wide variety of vapor samples. The preliminary experimental results for the detection of H_2O_2 in ambient air have been published.⁹⁾ The newly developed ion source and its function are described in detail in the following sections.

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2. Experimental

The conventional and the new type DBD ion sources are shown in Figs. 1(a) and (b), respectively. To generate the DBD plasma, a sinusoidal signal of 30 kHz from a function generator was amplified by a power amplifier and a transformer to several kV to generate a high AC voltage (H.V.). The discharge tube was made of a cylindrical quartz tube (*i.e.*, dielectric) with an inner diameter of 4 mm. The electrodes consisted of a stainless steel wire (inner electrode) and a copper strip (outer electrode). The outer copper strip electrode was attached to the outer surface of the quartz tube. The outer electrode was fed with the AC H.V. with respect to the inner electrode at ground potential. The outer end of the quartz tube was placed at a distance of 10 mm from the ion sampling orifice of the time-of-flight mass spectrometer (JEOL, AccuTOF, Akishima, Tokyo). DBD excited helium gas with flow rates of 0.2–0.5 L/min was directed toward the ion-sampling orifice. In the measurements, samples such as analyte-deposited cotton bud or a glass rod (10 mm in o.d.) were inserted between the space of the DBD quartz tube and the ion sampling orifice.

The ions were detected by a microchannel plate detector and measured by means of an analogue-to-digital-converter (ADC) (Fastflight Digital Signal Averager, ORTEC, Oak Ridge, Tennessee, U.S.A.).

3. Results and Discussion

3.1 Newly developed DBD ion source

The DBD ion source adopted in the early stages of our experiments is shown in Fig. 1(a). This type of DBD plasma has frequently been applied to surface chemical modification of organic and also inorganic materials in the field of material science.¹⁰⁾ As described above, this type of plasma source has also been adopted by several mass spectrometric research groups.^{4)–7)} In our preliminary experiments, this ion source gave relatively strong fragment ions, as well as secondary ions, the m/z values of which were higher than the molecular

weights of analytes when the plasma jet was exposed to the gaseous samples. The appearance of higher-mass ions may partly be due to the decomposition of the sample molecules followed by some complex secondary reactions that occur in the plasma.

In order to suppress the secondary processes that take place in the plasma, we developed a new-type of barrier discharge ion source that can cut off the plasma jet arising from the quartz tube. The new type DBD ion source is largely the same as the one shown in Fig. 1(a). The only difference is that the grounded inner wire electrode extends outside of the quartz tube as shown in Fig. 1(b). This seemingly minor modification made it possible to confine the DBD plasma inside the quartz discharge tube, resulting in an increase in the intensity of the molecular ion signals, with the ability to achieve soft ionization for various samples in the gaseous state. The reason for success in confining the plasma in the dielectric tube may be interpreted as follows.

Roughly speaking, there are two types of plasmas, thermal (hot) and non-thermal (cold) plasmas.³⁾ In the non-thermal plasma, the electron temperature (T_e) is much higher than the ion temperature (T_i) and the gas temperature (T_g), $T_e \gg T_i \approx T_g$. In the case of a non-thermal plasma such as a DC corona and barrier discharges, electronic excitation and ionization are one of the important processes taking place in the plasmas, due to the high T_e and low T_i and T_g . In contrast, in a thermal (hot) plasma such as an arc discharge, T_e is about the same as T_i and T_g , $T_e \approx T_i \approx T_g$. In such a thermal plasma, the fraction of electrons that have energies higher than the ionization energies of analytes are relatively small and thus mainly thermal degradation prevails in the plasma. Thus, for example, in an APCI experiment using a DC corona discharge, the transition from a corona discharge (non-thermal plasma) to an arc discharge (thermal plasma) by increasing the DC voltage applied to the needle electrode above the critical threshold value results in a drastic decrease in total ion signals.

Although DBD has attracted considerable interest only recently in the mass spectrometry field, DBD has been known for more than a century.¹⁰⁾ The merits for generating a cold plasma by a DBD discharge is as follows. The novel feature of DBD is that one of the electrodes is positioned outside the discharge space and is not in contact with the plasma (Fig. 1). In their pioneering work, Kanazawa *et al.* found that a “cold” non-equilibrium plasma can be generated at atmospheric pressure by DBD.¹¹⁾ DBD has a strong influence on local field distortions caused by a space charge accumulation on the dielectric. The dielectric that separates the two electrodes limits the discharge current due to charge accumulation on the dielectric. Thus the initially formed DBD ceases before the transition from glow discharge to arc discharge. In a sense, dielectric acts as a ballast that consumes minimum energy. This explains why thermal damage of the electrodes and dielectric is largely suppressed in DBD.

The reason why it is possible to confine the plasma jet in the dielectric tube by extending the inner wire electrode outside the quartz tube may be interpreted as follows. In DBD, a high-frequency AC voltage is ap-

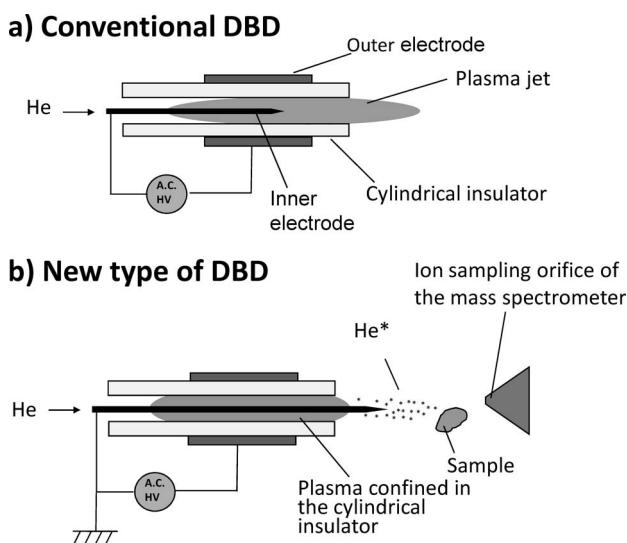


Fig. 1. Structures of the DBD ion sources. (a) Conventional DBD ion source. (b) New type of DBD ion sources.

plied to the two electrodes (Fig. 1). Thus, DBD involves the generation of an alternating field in the insulator tube. That is, the inner wall of the insulator tube becomes positively or negatively charged depending on the field applied between the two electrodes.

First, the case in which a positive potential is applied to the outer electrode relative to the central wire electrode in Fig. 1 is considered. As described above, T_e is much higher than T_i and T_g in the case of a low-temperature glow discharge plasma. In such a case, the insulator wall in contact with the glow discharge plasma is instantly charged with electrons, because electrons have much higher kinetic energies than ions. In contrast, the positive ions that hit the central wire electrode will escape to the earth because the central electrode is grounded. Thus, the glow discharge plasma cannot maintain its neutrality but becomes highly negative (*i.e.*, electron-rich), because relatively slow electrons cannot hit the wall but are reflected back in the plasma due to the space charge field generated on the negatively charged wall (*i.e.*, plasma sheath). As such, the plasma potential becomes highly negatively charged with the excess electrons. Thus, for the electrode shown in Fig. 1(a), a high electric field should be generated between the electron-rich plasma and the surrounding earth potential. Due to this high electric field, electrons in the plasma will be accelerated towards the surrounding ground-potential electrode (*i.e.*, the ion sampling orifice of the mass spectrometer) after exiting the insulator discharge tube. This should be the reason for the formation of a plasma jet extending out of the insulator tube. In this case, if the inner wire electrode is grounded and is extended outside the insulator tube, as shown in Fig. 1(b), the energetic electrons effusing out of the insulator tube must be attracted toward the grounded wire electrode as the result of the electric field generated between the plasma and the grounded electrode. The annihilation of energetic electrons just outside the insulator tube results in the plasma being confined to the inside of the insulator tube.

In the case where a negative potential is applied to the outer electrode relative to the grounded central wire electrode, the inner wall of the insulator tube is positively charged by the injection of positive ions generated in the plasma toward the insulator wall. On the other hand, electrons that hit the central electrode will escape to the earth, because the inner electrode is grounded. Thus, the plasma becomes positive-charge rich and an electric field should be generated between the plasma and the surrounding earth potential that accelerate the positive ions in the direction of the surrounding ground-potential electrode. In this case, however, a plasma jet is not generated, because the masses of the ions are much higher than that of an electron and ions exiting the insulator tube are quickly decelerated by the collisions with the ambient gas.

In sum, the DBD plasma jet extending from the insulator tube (Fig. 1(a)) should be generated only when a positive potential is applied to the outer electrode but it will diminish when an alternating potential is applied to the outer electrode. In other words, the plasma jet operates in a pulsed mode with the same frequency of

the AC field applied to the electrodes.

The ionization taking place in the ion source shown in Fig. 1(b) can be understood to be primarily based on gas-phase ion-molecule reactions (APCI) between analyte molecules and ambient air-based reagent ions, *e.g.*, N_4^+ ($N_2^+ + N_2 \rightarrow N_4^+$), O_2^+ , $[(H_2O)_n + H]^+$, $[\text{acetone} + H]^+$, *etc.* formed by a series of ion/molecule reactions initiated by the metastable helium atoms (He^*) (Penning ionization, internal energy of He^* : ~ 20 eV) that are generated by the DBD plasma. Protonated acetone often appeared as one of the major background signals under the experimental conditions of this study. This was due to the frequent use of acetone as a solvent in the laboratory.

Since the DBD ion source shown in Fig. 1(b) deals with the samples that are exposed to ambient air, the ionization conditions may be affected by the composition of air, which can change from moment to moment, *e.g.*, changes in relative humidity and contaminants in laboratory air. In the present experiments, however, no significant fluctuations in the experimental results were observed. This may be due to the fact that the product ions for the samples dealt with in this study are sufficiently stable and are less sensitive to the presence of impurities in ambient air. Namely, the analyte ions are likely to be terminal reaction products in a series of the ion/molecule reactions that take place under the present experimental conditions employed (see below).

3.2 Application of the DBD ion source to the detection of explosives

Using the discharge tube as shown in Fig. 1(b), soft ionization with little formation of fragment and higher-mass ions was realized for almost all of the vapor samples examined. As an example, the DBD mass spectrum of methyl stearate is shown in Fig. 2. In this measurement, powdered methyl stearate was placed on a cotton bud. The helium gas flowing out of the discharge tube was heated to about 120°C to promote the evaporation of the solid sample. In Fig. 2, the protonated molecular ion is observed as the major ion with only traces of fragment ions. The small peaks in the range of m/z 50–150 are background signals, because they appeared when no sample was introduced into the DBD ion source. In the electron ionization (EI) of methyl stearate, strong signals for fragment ions at

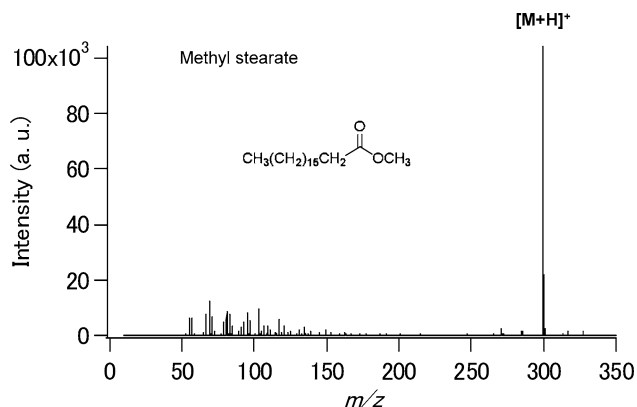


Fig. 2. Mass spectrum of methyl stearate obtained by using the ion source shown in Fig. 1(b).

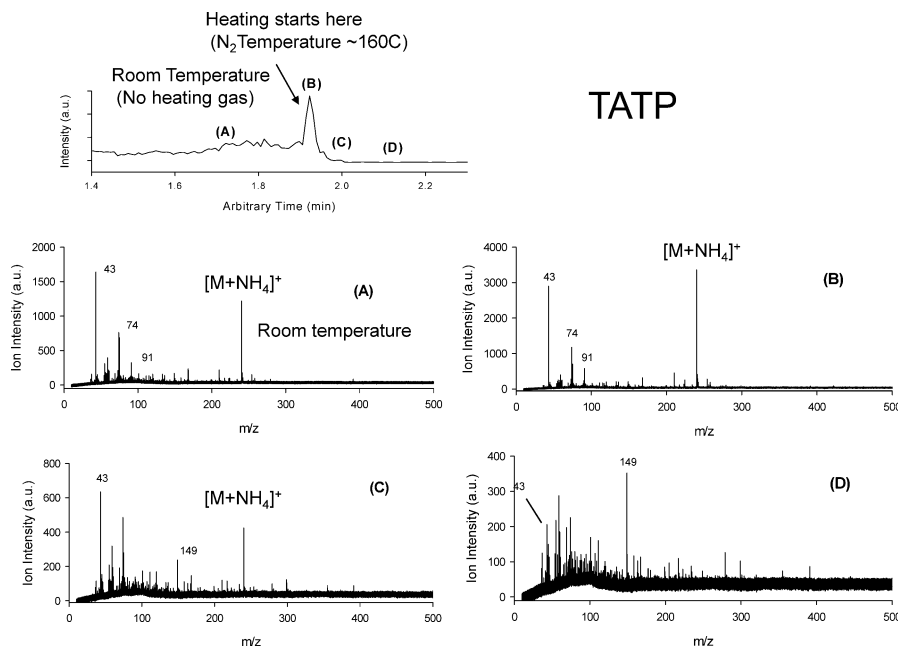


Fig. 3. Experimental results for 1 μ L of acetonitrile containing 1 ng of TATP deposited on a filter paper. Top panel: total ion current chromatogram. The sample was kept at room temperature from 0 to 1.9 min. At 1.9 min the heater of the barrier discharge tube was switched on and the temperature of the discharge tube was increased to 160°C within about 2 min. The mass spectra of (A), (B), (C), and (D) correspond to those measured at times of (A), (B), (C), and (D) shown in the total ion chromatogram.

m/z 43, 55, 74, 87, and 143 are observed, in addition to a molecular ion peak at m/z 300. These fragment ions, for example, the base peak at m/z 74 observed in the EI mass spectrum, are absent in Fig. 2.

Figure 3 shows the experimental results obtained for the improvised explosive, TATP. In this measurement, 1 μ L of acetonitrile containing 1 ng of TATP was deposited on a filter paper which was placed downstream from the discharge tube (see Fig. 1(b)). The mass spectra obtained are shown in Fig. 3(A). The peaks appearing at m/z 91, 74, and 43 are likely due to fragment ions of TATP, *i.e.*, $C_3H_7O_3^+$, $C_3H_6O_2^+$, and $C_2H_3O^+$, respectively. As shown in the figure, the ion signal at m/z 240 was found to be one of the major ions. This peak appeared only when the TATP sample was exposed downstream from the barrier discharge tube and its appearance was reproducible. We tentatively assigned this peak as a cluster ion comprised of TATP and an ammonium ion, $[TATP+NH_3+H]^+$. In this experiment, ammonia gas was not intentionally added in the operation. Therefore, we conjecture that the laboratory air may have been contaminated by trace amounts of ammonia. A conceivable source, for example, may be a spontaneous emission from the human body (*e.g.*, ammonia that is exhaled in the breath¹²).

The partial pressure of water vapor in ambient air should be much higher than that of the contaminant ammonia. In fact, protonated water cluster ions $[(H_2O)_n+H]^+$ were observed as major background ions but the ion signal for $[(H_2O)_n+NH_3+H]^+$ was negligible, compared to $[(H_2O)_n+H]^+$ under the present experimental conditions. Interestingly, however, the cluster ion $[TATP+H_2O+H]^+$ is absent in the mass spectra in Fig. 3. This suggests that the thermochemical stability of $[TATP+NH_3+H]^+$ is much higher than that of $[TATP$

$+H_2O+H]^+$. Cooks *et al.* carried out the rapid detection of trace amounts of TATP by desorption electrospray ionization (DESI).¹³ Significant ions in the positive ion DESI spectra were observed at m/z 240, 245, and 223, corresponding to $[TATP+NH_3+H]^+$, $[TATP+Na]^+$, and $[TATP+H]^+$, respectively, when a methanol/water solvent containing CH_3COONH_4 (10 mM) and NaCl (10 mM) was used for the electrospray solution. In the case of tandem mass spectrometry, the ion corresponding to $[TATP+NH_3+H]^+$ at m/z 240 undergoes a characteristic loss of 17 mass units (*i.e.*, NH_3) to give a fragment ion at m/z 223 $[TATP+H]^+$. This suggests that the proton affinity of TATP is nearly equal to or even larger than that of NH_3 (853.6 kJ/mol).¹⁴ The high proton affinity of TATP may be due to the fact that the binding cavity that is composed of oxygen atoms in cyclic peroxide TATP interacts with the proton in the cavity. Cooks *et al.* performed density functional theory (DFT) calculations for $[TATP+Na]^+$.¹³ The theoretical calculation predicted a very strong binding energy for $Na^+\cdots TATP$ of 196 kJ/mol. In $Na^+\cdots TATP$, the sodium ion is calculated to be centered in and slightly above the binding cavity and equidistance from the oxygen atoms. The determination of the structures and stabilities of $[TATP+NH_3+H]^+$ and $[TATP+H]^+$ is of fundamental interest and further studies are ongoing in our laboratory.

As shown in Fig. 3(A), TATP was detected at room temperature (without heating the helium gas flowing from the discharge tube). The detection of TATP is straightforward due to its high vapor pressure, ~ 5 Pa at room temperature. The upper panel in Fig. 3 shows data on the ion signal intensity of $[TATP+NH_3+H]^+$ as a function of time. The signal intensity remains nearly constant from 0 to 1.9 min. At 1.9 min the

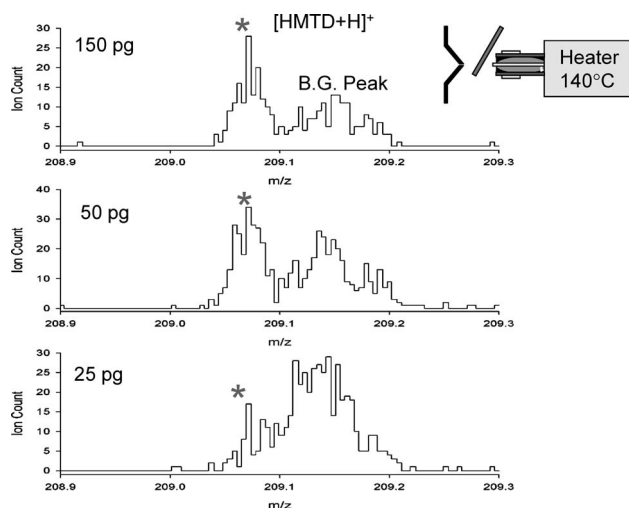


Fig. 4. Experimental results obtained for HMTD with 150, 50, and 25 pg dissolved in 0.5 μ L acetone deposited on the surface of a glass rod (10 mm o.d.) with a spot size of \sim 2 mm. The ions detected by the multi channel plate detector were converted to the digital signals by a 4 GHz time-to-digital-converter (TDC).

heater of the barrier discharge tube was switched on and the temperature of the discharge tube was increased to 160°C in about 2 min. As shown in the upper panel at (B), a sudden increase in the ion signal intensity was observed. The signal intensity decreased to the background level within \sim 2 min, due to depletion of the sample.

Hexamethylene triperoxide diamine (HMTD) is also a material used as an improvised explosive and is much more difficult to detect than TATP because of its low vapor pressure. The vapor pressure of HMTD at room temperature is not known because it is too low to measure. The vapor pressure at higher temperature is also not known because of thermal decomposition.¹⁵⁾ In this experiment, we deposited known amounts of HMTD dissolved in 0.5 μ L acetone on the surface of a glass rod (10 mm o.d.) with the spot size of \sim 2 mm. In such a sample preparation, almost all of the sample can be interrogated by the present DBD ionization system, because of the small sample spot size. In this measurement, the ions detected by the MCP were converted into the digital signals by a 4 GHz time-to-digital-converter (TDC) in order to determine the limit of detection for HMTD. Although TDC has a smaller dynamic range for the signal response, it is more sensitive than ADC.

No ion signals for HMTD were detected at room temperature when 1 ng of HMTD deposited on a glass rod was exposed just outside of the DBD ion source. However, protonated HMTD, $[\text{HMTD} + \text{H}]^+$, could be easily detected by heating the barrier discharge ion source to about 140°C. The temperature of 140°C was adopted because HMTD begins to decompose above this temperature. Figure 4 displays the mass spectra of HMTD with sample amounts of 150, 50, and 25 pg deposited on a glass rod that was exposed to the DBD excited heated helium gas just outside of the insulator discharge tube. Although the background ion signal

appears at $m/z \sim 209.16$, protonated HMTD, $[\text{HMTD} + \text{H}]^+$, could be detected at m/z 209.07, as shown in Fig. 4. The limit of detection was determined to be about 25 pg.

In a separate experiment, we performed an analysis of HMTD using LC/MS equipped with electrospray. The apparatus used was a Waters 2690, Micromass ZMD instrument, with a Waters Symmetry C18 column, ESI: $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (6/2/92). The limit of detection was determined to be about 50 pg for HMTD. This value is about the same as that obtained by LC/MS equipped with an APCI ionization source.¹⁶⁾ That is, the present barrier discharge ion source is as sensitive as methods using standard LC/MS techniques. Another advantage of the present method is that no special sample preparation is necessary.

4. Conclusion

A new type barrier discharge ion source was developed. In this method, the DBD plasma is confined in the dielectric discharge tube and terminates at the outer end of the dielectric discharge tube. Thus, gaseous analyte molecules are ionized just outside of the barrier discharge tube without being exposed to the plasma. This permits soft and high-sensitive ionization for the detection of explosives, e.g., the limit of detection for the improvised explosive HMTD was determined to be 25 pg. The DBD ion source developed in this study has the potential to become a high-sensitive and versatile technique for use in the area of ambient mass spectrometry.

Acknowledgments

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