

# Direct detection of explosives on solid surfaces by mass spectrometry with an ambient ion source based on dielectric barrier discharge

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Trace amounts of explosives on solid surfaces were detected by mass spectrometry at ambient conditions with a new technique termed dielectric barrier discharge ionization (DBDI). By the needle–plate discharge mode, a plasma discharge with energetic electrons was generated, which could launch the desorption and ionization of the explosives from solid surfaces. Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4,6-trinitrotoluene (TNT), and pentaerythritol tetranitrate (PETN) were desorbed directly from the explosives-contaminated surface by DBDI, forming the typical anions of  $[\text{TNT}]^-$ ,  $[\text{TNT} - \text{H}]^-$ ,  $[\text{RDX} + \text{NO}_2]^-$ ,  $[\text{PETN} + \text{ONO}_2]^-$ , and  $[\text{RDX} + \text{ONO}_2]^-$ . The ions were transferred into the MS instrument for analysis in the negative ion mode. The detection limit of present method was 10 pg for TNT ( $m/z$  197, S/N 8:1), 0.1 ng for RDX ( $m/z$  284, S/N 10:1), and 1 ng for PETN ( $m/z$  260, S/N 12:1). The present method allowed the detection of trace explosives on various matrices, including paper, cloth, chemical fiber, glass, paints, and soil. A relative standard deviation of 5.57% was achieved by depositing 100 pg of TNT on these matrices. The analysis of A-5, a mixture of RDX and additives, has been carried out and the results were consistent with the reference values. The DBDI-MS method represents a simple and rapid way for the detection of explosives with high sensitivity and specificity, which is especially useful when they are present in trace amounts on ordinary environmental surfaces. Copyright © 2007 John Wiley & Sons, Ltd.

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**KEYWORDS:** dielectric barrier discharge ionization (DBDI); ion source; explosives; direct desorption and ionization; negative ion mode

## INTRODUCTION

Sensitive and specific detection of explosives is an important analytical issue, since explosives from military and industrial sources, as well as improvised explosive devices, have been used worldwide in terrorist events. Furthermore, the explosives-related compounds must be monitored in soil, groundwater, and surrounding waterways since these mutagenic, toxic, and persistent pollutants can leach from the contaminated soil to accumulate in the food chain.<sup>1</sup> As a result, there is a high demand for developing highly sensitive methods for the real-time detection of explosives and explosive-related compounds with a low false alarm rate.

A wide variety of methods have already been developed and used to detect explosives under various conditions including ion mobility spectrometry (IMS),<sup>2</sup> gas chromatography,<sup>3</sup> near-field optical microscopy,<sup>4</sup> voltammetric method,<sup>5</sup> polymer sensor,<sup>6</sup> immunoassay,<sup>7</sup> and mass

spectrometric methods.<sup>8–15</sup> It should be noted that mass spectrometric methods, such as electrospray ionization (ESI),<sup>8,9</sup> single-particle aerosol mass spectrometry,<sup>10</sup> atmospheric pressure chemical ionization (APCI),<sup>11–13</sup> and laser time-of-flight related methods,<sup>14</sup> are important tools for the detection of explosives. These mass spectrometric methods offer the advantages of high sensitivity, short response time, as well as the additional selectivity available from MS/MS and ion/molecule reactions. However, these methods generally require sample preparation, and direct detection of explosives presented on solid surfaces can be problematic because of low vapor pressure and thermal instability of explosives. In addition, the limited sample size, deliberate concealment, and its co-occurrence with interfering compounds make trace and residue explosives analysis on surfaces more difficult.<sup>15,16</sup>

Several ionization methods have been reported for the direct ionization of explosives on solid surfaces, such as atmospheric pressure matrix-assisted laser desorption/ionization (MALDI),<sup>17</sup> secondary ion mass spectrometry (SIMS),<sup>15</sup> thermal desorption mass spectrometry,<sup>18,19</sup> and glow discharge

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ionization.<sup>20</sup> But those ion sources require the analytes to be exposed to elevated temperatures, ultraviolet irradiation, laser radiation, high-velocity gas stream, or reduced pressure conditions.<sup>21</sup> Recently, a family of new ion sources has been proposed, which allows ions to be created under ambient conditions and then collected and analyzed by MS, which are intended to be used for rapid detection of explosives from a complex matrix without sample workup. Ambient ionization techniques have been employed for the direct sampling and ionization of explosives desorbed on surfaces, such as direct analysis in real time (DART)<sup>21,22</sup> and desorption electrospray ionization (DESI).<sup>16,23–25</sup>

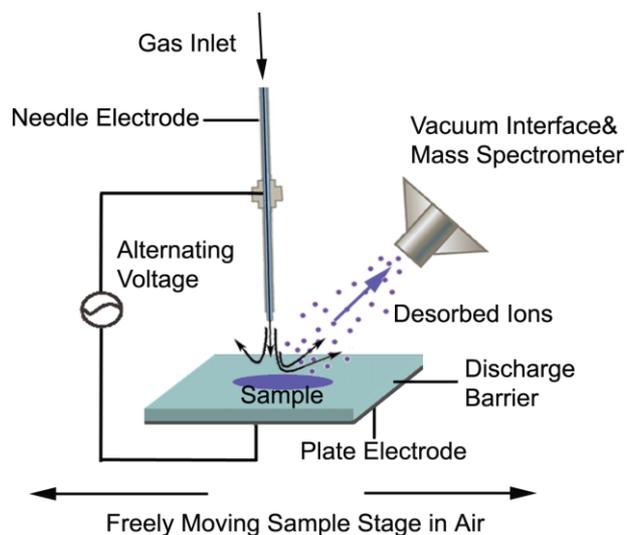
In our lab, another type of direct desorption/ionization technique for mass spectrometry, dielectric barrier discharge ionization (DBDI), was proposed for the detection of amino acids from solid surfaces without any sample preparation at ambient conditions.<sup>26</sup> This technique is based on the production of 'cold' nonequilibrium plasma of DBD with the ease of atmospheric-pressure operation to generate the analyte ions. DBD is composed of a dielectric layer inserted between two electrodes and can be obtained at ambient pressure with a.c. operation.<sup>27</sup> The dielectric limits the average current density in the gas space, forming a stable, low-temperature plasma (slightly above the room temperature) with high energetic electrons. Analytes can be desorbed and ionized from the surface by ion bombardment through the plasma sheath formation. Without the electrosprayed solvent such as DESI, and complex structures as DART, the very simple ionization source has the characteristics of small size with the ease of operation, which could potentially be coupled to portable mass spectrometers.

In this paper, the detection of explosives has been achieved by the DBDI ion source coupled to mass spectrometry in the negative ion mode. The explosives 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and pentaerythritol tetranitrate (PETN) were desorbed and ionized directly from solid surfaces. The typical anions were confirmed and the fragmentation routes were demonstrated by the data of MS. In addition, TNT deposited on various matrices has been detected for demonstrating the ability of present method to be used for the determination of trace explosives on complex matrices.

## EXPERIMENTAL

### DBDI ion source

Our DBDI ion source is illustrated in Fig. 1. A hollow stainless steel needle (0.3 mm i.d. × 60 mm) acts as one electrode, and a piece of copper sheet (10 × 10 mm) as the other. A glass slide (30 × 30 × 1 mm) is inserted between the two electrodes and placed on the surface of a copper sheet. The glass slide not only serves as a discharge barrier, but also provides a specimen stage for the samples. Gas flows through the needle at a flow rate of 50–200 ml/min, which is controlled by a flow meter. The distance between the needle tip and the surface of the glass slide is 5–10 mm, and the angle is in the range of 80–90°. Power supplies (6 × 4 × 3 cm, Beili Guoke Co. LTD, Beijing, China) are connected to



**Figure 1.** The schematic diagram of DBDI ion source.

the electrodes, and an alternating voltage of 3.5–4.5 kV at frequencies of 18.0–25.0 kHz is applied for the generation of an atmospheric-pressure plasma. The glass slide and copper sheet are mounted on a 3D moving stage, allowing them to be positioned at any chosen point with respect to the plasma between the two electrodes. The analytes on the surfaces are sequentially located in the field of plasma discharge for desorption and ionization. (The ionization mechanism is shown in Supporting Information.) The ions are introduced into the mass spectrometer for detection. The distance between the DBDI source and the vacuum interface of the mass spectrometer is 20–30 mm. Ions are detected with a commercial ion-trap mass spectrometer (Finnigan LTQ, Thermo Electron Corp., San Jose, CA). Data are processed using the instrument software interface (Xcalibur version 1.4 SR1). The mass spectrometry conditions are as follows: source voltage (applied to the spray capillary) 0 kV; tube lens voltage –95 V; capillary temperature 275 °C; heated capillary voltage –33 V; multipole r.f. amplitude ( $V_{p-p}$ ) 400 V; and multiplier voltages 1 and 2, –1200 V. The ion injection time is set to 50 ms, and the number of microscans is set to one. A total spectral acquisition time of 3 s is used.

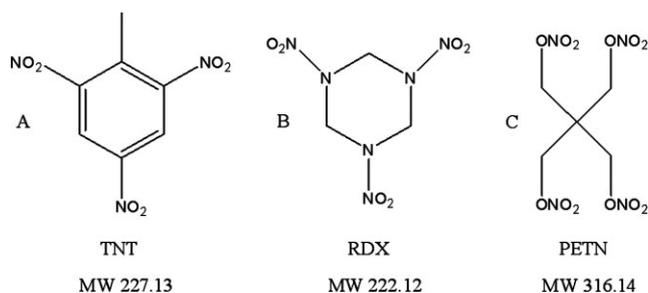
### Chemicals and reagents

All reagents were of analytical reagent grade. Acetone, ethanol,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{COOH}$ , NaCl,  $\text{NH}_4\text{Ac}$ ,  $\text{NH}_4\text{Cl}$  and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co. Ltd (Beijing, China). Water was deionized and further purified with a Milli-Q water purification system (Millipore, Milford, MA). Helium (99.998%) from Huayuan Gas (Beijing, China) was used as the carrier gas. The explosives, TNT, RDX, PETN, and the mixed explosive A-5, were dissolved in acetone to the appropriate concentrations.

## RESULTS AND DISCUSSION

### Desorption and ionization of explosives on surfaces

Most of explosives exhibit high electron affinities associated with the nitro- or nitrate functional groups, indicating that they readily form negative ions by electron capture.<sup>15</sup> TNT,



**Figure 2.** Chemical structures of 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and pentaerythritol tetranitrate (PETN).

**Table 1.** Explosives analysis results

| Explosive | Ions observed | Assignment   |
|-----------|---------------|--|
| TNT       | 227 (32%)     | [M] <sup>-</sup>   |
|           | 226 (72%)     | [M - H] <sup>-</sup>   |
|           | 197 (100%)    | [M - NO] <sup>-</sup>  |
| RDX       | 284 (100%)    | [M + NO <sub>3</sub> ] <sup>-</sup>  |
|           | 268 (28%)     | [M + NO <sub>2</sub> ] <sup>-</sup>  |
| PETN      | 378 (100%)    | [M + NO <sub>3</sub> ] <sup>-</sup>  |
|           | 260 (88%)     | [M - H + H <sub>2</sub> O - NO <sub>2</sub> CHCH <sub>2</sub> ] <sup>-</sup> |

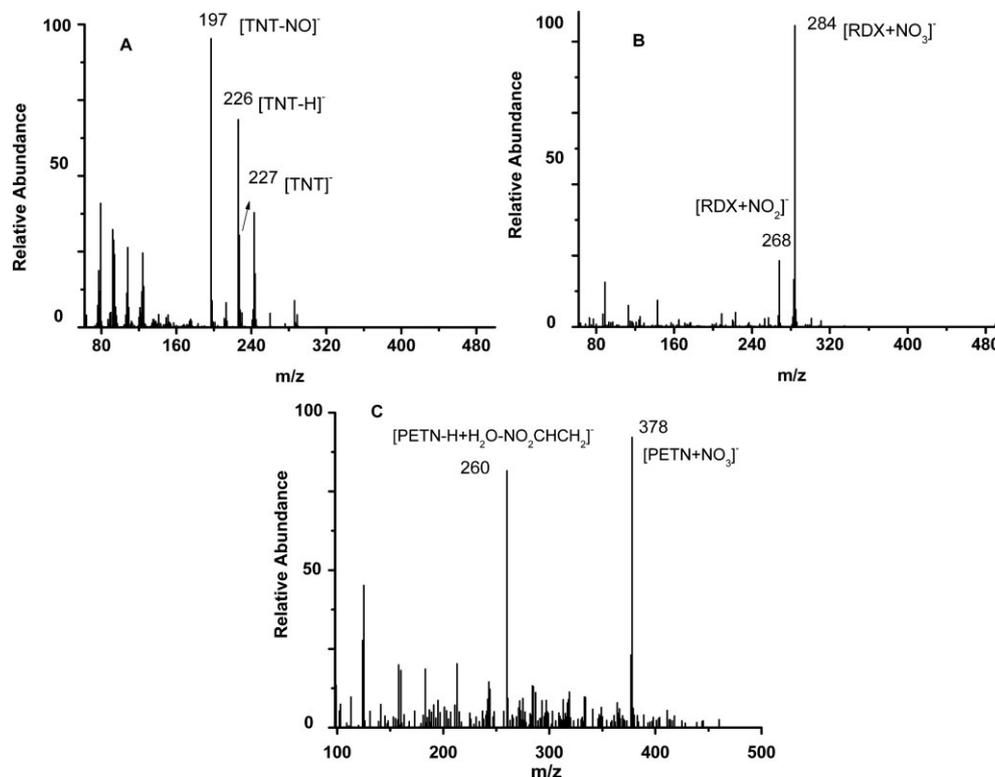
RDX, and PETN are common explosives and were selected for analysis based on their structural classes: nitroaromatic, nitramine, and nitrate ester, respectively (Fig. 2).

In our preliminary experiments, TNT, RDX and PETN were deposited individually on a piece of filter paper about

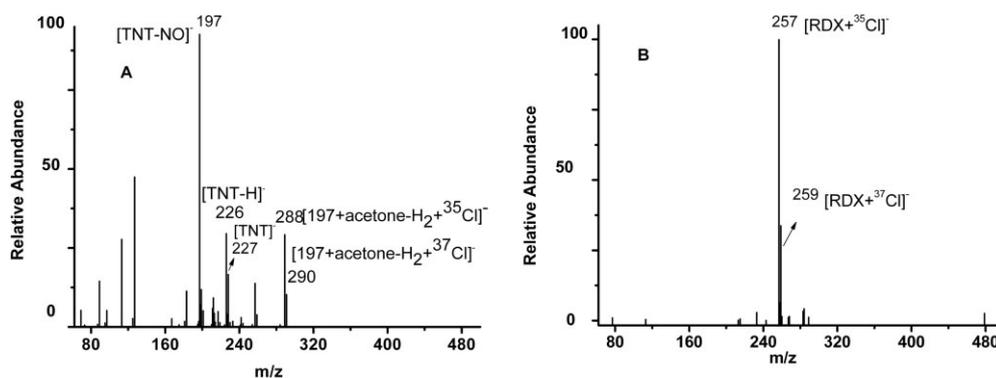
0.5 × 0.5 cm. It was then placed on the glass slide for desorption and ionization by DBDI. As shown in Fig. 3, all the explosives were well desorbed and ionized as negative ions from the surface. The characteristic ions of TNT are attributed to [TNT]<sup>-</sup>, [TNT - H]<sup>-</sup> and [TNT - NO]<sup>-</sup> (Fig. 3(A)). [M + NO<sub>2</sub>]<sup>-</sup> and [M + NO<sub>3</sub>]<sup>-</sup> were the characteristic ions of RDX (Fig. 3(B)) and PETN (Fig. 3(C)). All the results are summarized in Table 1.

### Adduct formation in the detection of explosives

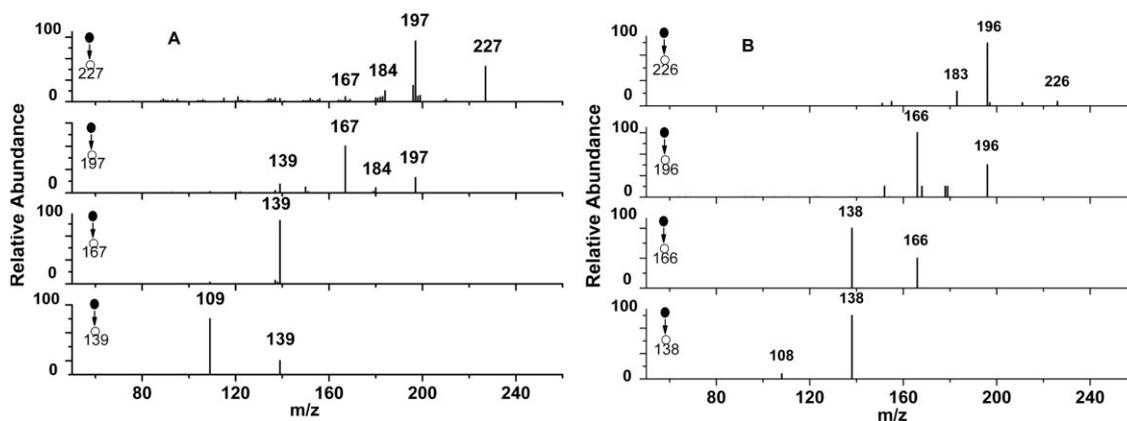
Negative ion mode was generally chosen for detecting the deprotonated molecular ion [M - H]<sup>-</sup>. However, addition of an organic acid or salt is necessary to form adduct ions for cyclic nitroamine explosives, such as RDX, because of the lack of acidic protons.<sup>9</sup> Hydrochloric acid, sodium chloride, acetic acid, ammonium nitrate, ammonium chloride, and chloroform are commonly used as additives to form stable adducts ions with the explosives.<sup>9,11–13,15,23</sup> Therefore, those additives were examined in the present work and the results showed that hydrochloric acid, chloroform, acetic acid, and ammonium acetate could form stable adducts with explosives in DBDI-MS. Taking the adducts of hydrochloric acid with TNT and RDX as examples, the ions of [TNT - NO + acetone - H<sub>2</sub> + <sup>35</sup>Cl]<sup>-</sup> (*m/z* 288) and [RDX + <sup>35</sup>Cl]<sup>-</sup> (*m/z* 257) are characterized by the presence of isotopes [TNT - NO + acetone - H<sub>2</sub> + <sup>37</sup>Cl]<sup>-</sup> (*m/z* 290) and [RDX + <sup>37</sup>Cl]<sup>-</sup> (*m/z* 259), respectively, with one-third the abundance (Fig. 4). However, remarkable increases for the sensitivities of the explosives have not been achieved by using the additives.



**Figure 3.** Mass spectra of explosives in negative ion mode of DBDI: (A) TNT, (B) RDX, (C) PETN. The explosive was deposited on 0.5 × 0.5 cm of filter paper with total amount of 10 ng.



**Figure 4.** Mass spectra of TNT (A) and RDX (B) when doped with hydrochloric acid (0.05%). The acetone solutions containing 10 ng of each explosive were mixed with hydrochloric acid, before being dropped on the surface of glass slide.



**Figure 5.** MS<sup>n</sup> mass spectra of TNT in the negative ion mode by DBDI-MS. (A) MS<sup>n</sup> of TNT with  $m/z$  227, (B) MS<sup>n</sup> of TNT with  $m/z$  226.

### Fragmentation patterns of explosives by MS<sup>n</sup> spectra

The MS<sup>n</sup> spectra of the explosives were obtained by collision-induced dissociation (CID) to explore the relationship between their fragmentation patterns and structural features. The MS<sup>n</sup> spectra of TNT are shown in Fig. 5(A). It is demonstrated that  $m/z$  197 involves the loss of NO from the molecular anion of  $m/z$  227. The ion at  $m/z$  167 is the product ion by losing NO from the fragment ion of  $m/z$  197. The ion at  $m/z$  139 is achieved by losing CO from  $m/z$  167. Furthermore,  $m/z$  139 can produce  $m/z$  109 by losing NO. This course can be explained by the presence of the hydrogen ion *ortho* to NO<sub>2</sub> group in the benzene ring.<sup>28–30</sup> Thus, the fragment series of TNT were proposed (Fig. S-1). In addition, it is interesting that for  $m/z$  226 similar fragmentation patterns were observed (Fig. 5(B)).

### The optimization of ionization parameters Description with different arrangements of the DBD electrode

TNT was selected as the mode for the optimization of discharge parameters to improve the signal/noise ratio. Two atmospheric discharge modes, the needle–plate discharge mode and co-planer surface discharge mode, were investigated for detecting 100 pg of TNT. By the needle–plate discharge mode, the typical ions of  $m/z$  197, 226, and 227 were observed (Fig. 6(A)), while, only a low abundance of  $m/z$  197

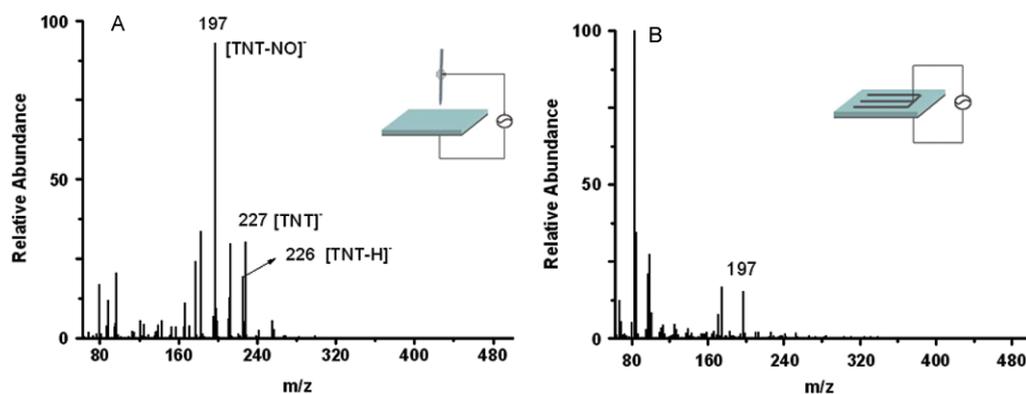
was observed by the co-planer surface discharge (Fig. 6(B)). This result indicates that the needle–plate discharge is more effective. Therefore, the needle–plate discharge mode was selected to form the DBDI ion source in our work. In addition, needle–plate mode gave a thin thread plasma that could concentrate in the micro-area of the surfaces, which potentially could be used for imaging analysis.

#### Effect of discharge gases

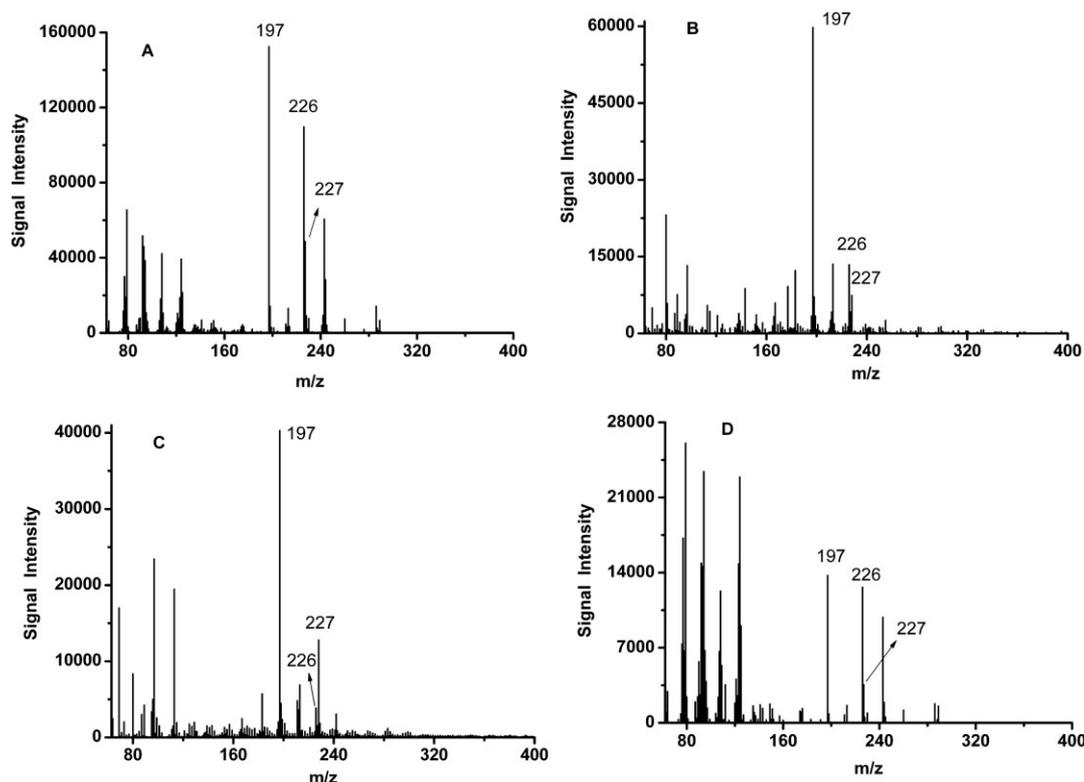
DBD can be generated by He, N<sub>2</sub>, Ar, and even air.<sup>2</sup> Therefore, four types of discharge gases, helium, nitrogen, argon and air, were tested for the detection of TNT in the present work. As shown in Fig. 7, the highest signal intensity of assignment ions for TNT could be achieved by helium at the same flow rate.

#### Effect of gas flow rate

The gas flow rate is an important factor for obtaining the DBD discharge plasma, which can be varied from several hundred milliliters to several liters per minute.<sup>31</sup> In our studies, a gas flow rate of 50–200 ml/min was sufficient to maintain a stable discharge for obtaining the typical ions. The highest signal/noise ratio was obtained at the flow rate of 150 ml/min (about 35 m/s), which was therefore used in the subsequent procedure. The mass spectra obtained at different flow rates (0, 50, 100, 150, 200 ml/min) are shown in Fig. S-2. Even on decreasing the gas flow rate to zero, the



**Figure 6.** Comparison of two types of electrode arrangements for the desorption and ionization of 100 pg TNT. (A) Needle-plate mode; (B) Co-planer surface discharge mode. The insets show schematic diagrams of two types of the electrode arrangements.



**Figure 7.** Mass spectra of TNT obtained by different discharge gas. (A) He, (B) N<sub>2</sub>, (C) Ar, (D) air. The gas flow rate was 150 ml/min. An amount of 10 ng of TNT was deposited on the surface of a filter paper with an area of about 0.5 × 0.5 cm.

typical ions of  $m/z$  197, 226, and 227 could still be observed. In comparison with those in DESI (>350 m/s)<sup>24</sup> and DART (1500–3000 ml/min),<sup>21</sup> the flow rate adopted in present work is much lower.

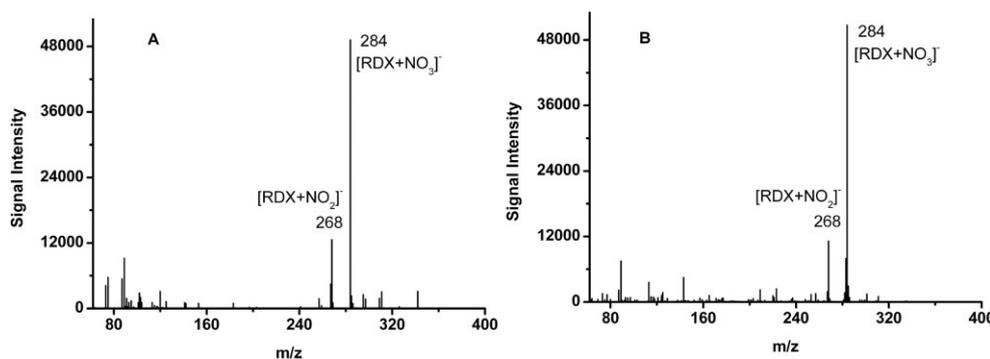
#### Effect of the discharge power

The effect of the discharge power on the detection of explosives in the negative ion mode was examined in our work. By increasing the power from 5 W to 30 W, the signal intensities of  $m/z$  197 and 227 were increased about sevenfold and fourfold (Fig. S-3). Further increase of the discharge power may cause elevated temperature, leading to the breakdown of the glass slide. Thus an ionization power of 30 W was adopted in our study. It may be noted that the power supply of 30 W costs only about US\$5 with the

size of 6 × 4 × 3 cm, and is commercially available as ozone generator in the market.

#### Analytical performance

To evaluate the performance of the present method on various matrices, 100 pg of TNT was deposited on paper, cloth, chemical fiber, glass, paints, and soil. As shown in Fig. S-4, the signal intensities of  $m/z$  197 on different matrices are 1.75, 1.88, 1.92, 1.64, 1.80, and 1.81 × 10<sup>4</sup>, which results in a relative standard deviation (RSD) of 5.57%. The results indicated that there was no significant difference for the detection of TNT on various matrices. The LOD was 10 pg for TNT ( $m/z$  197, S/N 8:1), 0.1 ng for RDX ( $m/z$  284, S/N 10:1), and 1 ng for PETN ( $m/z$  260, S/N 12:1). It has been reported that the detection limit of explosives by IMS, the



**Figure 8.** Mass spectra of (A) A-5 and (B) RDX.

standard technology, is 70 pg for TNT, 300 pg for RDX, and 80 pg for PETN.<sup>32</sup> Thus, the DBDI method has a sensitivity similar to IMS for the detection of TNT and RDX.

### Sample analysis

To examine the DBDI method in a real sample analysis, a mixed explosive, A-5, was detected from the surface of the glass slide. The typical anions of  $m/z$  268 and 284 were obtained from the mass spectra of 10 ng A-5 (Fig. 8(A)). Compared with the mass spectra of 10 ng of pure RDX (Fig. 8(B)), it is confirmed that the RDX was the main component in A-5 (97.0% for  $m/z$  284 and 113.3% for  $m/z$  268), which is consistent with the reference values.<sup>33</sup>

### CONCLUSIONS

Trace amounts of explosives on solid surfaces of various matrices including paper, cloth, chemical fiber, glass, paints, and soil have been detected by DBDI-MS at ambient conditions without any sample preparation. This method is demonstrated to be highly sensitive for the detection of explosives from picogram to nanogram range, which is comparable with that of DART and DESI. In addition, the flow rate of the carrier gas is about 10 times lower compared to that of DART and DESI. With the low cost, small and simple device, the DBDI ion source can be coupled to portable mass spectrometers, which may be potentially used for the fast detection of explosives in the field of antiterrorism and environmental conservation.

### Supplementary material

Supplementary electronic material for this paper is available in Wiley InterScience at: <http://www.interscience.wiley.com/jpages/1076-5174/suppmat/>.

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