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COMMUNICATION

Water-Assisted Low Temperature Plasma Ionization Source for Sensitive Detection of Explosives

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A water-assisted low temperature plasma (WALTP) ionization source based on a quartz T shaped tube was developed for a miniature rectilinear ion trap mass spectrometer to sensitively detect explosives at low picogram level. By introducing wet air into the plasma stream through the side tube, the explosives responses and repeatability were improved, and the mass spectra were simplified.

Sensitive detection of explosives is an important topic involving fields of security services, forensic investigation, and environmental analysis.[1] In most practical explosives analysis cases, the sensitivity and repeatability are extremely essential. Various techniques have been developed for explosives detection, such as Raman spectroscopy,[2] ion mobility spectrometry,[3] and mass spectrometry (MS).[4] Among these methods, MS has been regarded as an effective technique with the features of high sensitivity, high specificity, and rapid analysis speed; furthermore, the appearance of miniature instruments like rectilinear ion trap mass spectrometer (RIT-MS) equipped with discontinuous atmospheric pressure interface (DAPI) and ambient desorption/ionization (ADI) sources expands the applications of MS to the field of on-site analysis.[5]

ADI sources for MS are able to ionize the analyte without sample pretreatment, which have enabled the rapid and sensitive detection of explosives.[6] Up to now, more than thirty kinds of ADI techniques have been developed, *e.g.*, desorption electrospray ionization (DESI),[7] flowing atmospheric-pressure afterglow (FAPA),[8] direct analysis in real time (DART),[1a, 9] and low temperature plasma (LTP).[10] The LTP has been successfully applied to detect organic and inorganic explosives, including trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), pentaerythritol tetranitrate (PETN), and black powder.[6c, 10a] By merging discharge gas with trifluoroacetic acid (TFA) vapor, a “reactive” LTP mode was adopted to enhance the specificity for RDX and cyclo-1,3,5,7-tetra-methylenetetranitrate (HMX) detection due to the formation of additional adduct ions $[M+TFA]^-$.[6b] However, as the TFA vapor was flowed through the discharge electrodes, it might cause the corrosion of electrodes and shorten the life expectancy of the LTP source. Recently, a reactive LTP array was capable of avoiding the corrosion of electrodes by the introduction of trifluoroacetic anhydride into the plasma plume through a separated stainless steel capillary.[11] Nevertheless, the detection sensitivity was not improved via the reactive LTP, and the use of toxic TFA or trifluoroacetic anhydride in the open ambient might harm the operators of the apparatus, which limited their application.

Herein, a safe, environment-friendly, and novelly-constructed water-assisted low temperature plasma (WALTP) ionization source was developed to improve the sensitivity and simplify the mass spectrum for explosives detection, on the basis of no corrosion for electrodes. The limits of detection (LODs) and repeatability were evaluated, and a mixture of explosives was measured to demonstrate the capability of this ionization source for the analysis of complex explosive samples.

In this study, explosives deposited on the polytetrafluoroethylene (PTFE) swab were heated by a halogen lamp; the thermally desorbed sample molecules were then ionized via a WALTP torch and analyzed by a home-made miniature RIT-MS, as shown in Fig. 1. The WALTP utilized dielectric barrier discharge (DBD) to create nonequilibrium plasma with temperature of about 30 °C.[12] The WALTP torch, with total length of 150 mm, was fabricated by a quartz T shaped tube (6 mm o.d. and 4 mm i.d.). The distances from the side tube to the end of WALTP torch and the overlap of discharge electrodes (the position of discharge region) were both 15 mm. A stainless steel cylinder (6.3 mm o.d. and 6.1 mm i.d.) set outside of the tube and a stainless steel rod (1.57 mm o.d.) centered axially were employed as the high voltage (HV) electrode and the internal electrode, respectively. A PVM500 Plasma Resonant Driver (Information Unlimited, New Hampshire, USA) provided an alternating voltage, 1.6 KV_{p-p} at a frequency of 25 KHz, to the HV electrode while the internal electrode was grounded, generating the dielectric barrier discharge. Helium was used as the discharge gas, with a flow rate of 150 mL min^{-1} for RDX and PETN detection, while that of 100 mL min^{-1} for 2,4,6-trinitrophenylmethylnitramine (tetryl). Instead of passing through the discharge electrodes, the wet air with a flow rate of 25 mL min^{-1} was introduced into the plasma stream via a side tube, avoiding the corrosion of discharge electrodes. The wet air was prepared by bubbling through purified water, and its relative humidity was 100% measured by a dew point sensor (DP300, CS Instrument GMH). The dimension of miniature RIT-MS was 38×34×26 cm and its total weight was 20 kg. The mass range of RIT-MS was *m/z* 70-600. The detail analytical procedure and the configuration of RIT-MS were described previously.[6c]

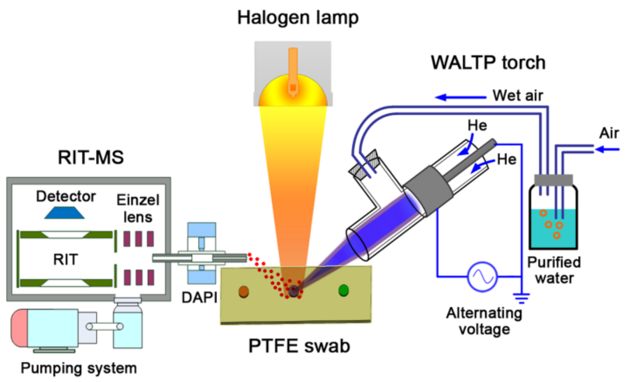

Fig. 1 Schematic of the explosives detection platform consisting of a water-assisted low temperature plasma (WALTP) torch, a halogen lamp, and a rectilinear ion trap mass spectrometer.

Three samples, 0.5 ng RDX, 0.5 ng PETN, and 0.5 ng tetryl, were tested to estimate the analytical performances of WALTP for the explosives analysis. As a comparison, these explosives were also measured when the side tube of WALTP was sealed (equal to the conventional LTP[6c]). As illustrated in Fig. 2, the mass spectra of RDX and PETN are characterized by nitro adducts of $[M+NO_2]^-$ and $[M+NO_3]^-$, while the mass spectrum of tetryl is characterized by $[Tetryl+NO_3]^-$; $[HNO_3+NO_3]^-$ is the dominant reactant ion in the WALTP. From Fig. 2, it is clear that the use of WALTP brings an enhancement for $[M+NO_3]^-$ intensities, about 3-fold (RDX), 2-fold (PETN), and 2-fold (tetryl) respectively as high as those obtained by the conventional LTP. Moreover, the mass spectra obtained by the WALTP are much cleaner. The relative intensities for $[RDX+NO_2]^-$ and $[PETN+NO_2]^-$ are decreased, and the intensities of fragment ions for tetryl[6b] are reduced to about one-fifth (*m/z* 181), two-fifths (*m/z* 210), one-eighth (*m/z* 241), and one-fourth (*m/z* 257) respectively of those obtained by the conventional LTP. It has been reported that the ionization of 2,4-dinitrotoluene would form the deprotonated ion (*m/z* 181) by the conventional LTP, while that of TNT would form the fragment ion with *m/z* of 210.[6b, c] Therefore, the mass peaks for fragment ions of tetryl (with *m/z* of 181 and 210) would overlap with those for the deprotonated ion of 2,4-dinitrotoluene and fragment ion of TNT. Encouragingly, the reduction of fragment ions for tetryl by the WALTP would avoid the serious overlap of mass peaks for different explosives and simplify the mass spectrum, which is a benefit for the qualitative and quantitative analysis of mixed explosives.

The detail mechanism for the reduction of fragment ions using the WALTP torch needs further study, so only a preliminary deduction is given below. First, the increased $[HNO_3+NO_3]^-$ ions in the WALTP ionization source (shown in Fig. 3) were easier to react with explosives to form stable $[M+NO_3]^-$ ions than the reactant ions NO_3^-, as the extra reaction heat could be taken away by neutral molecules HNO_3, which would avoid their further fragmentation. Second, the introduction of H_2O molecules might decrease the amount of metastable species in the plasma, which might avoid the dissociative ionization of explosives.

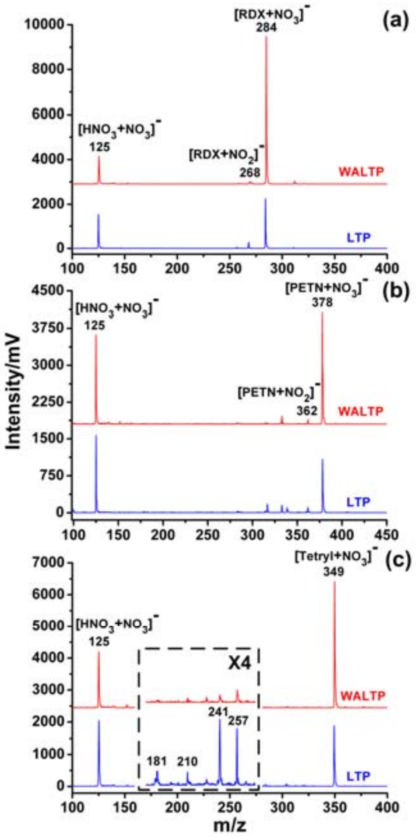

Fig. 2 Mass spectra of (a) 0.5 ng RDX, (b) 0.5 ng PETN, and (c) 0.5 ng tetryl obtained by the WALTP torch and with its side tube sealed (equal to the conventional LTP source), respectively.

To investigate the reasons for the response improvement of explosives by the WALTP, the mass spectra of reactant ions for the WALTP and conventional LTP were recorded, respectively. Since the low mass cut-off of the RIT-MS was *m/z* 70, this experiment was implemented by an atmospheric pressure time-of-flight mass spectrometer. As demonstrated in Fig. 3, the intensity of $[HNO_3+NO_3]^-$ for the WALTP is about 3 times as high as that for the conventional LTP, while the intensities of NO_3^- are almost equal for both ionization sources, and the intensity of NO_2^- is decreased in the WALTP. Apparently, the enhancement factor of $[HNO_3+NO_3]^-$ intensity is approximately corresponding to that of $[M+NO_3]^-$ intensity for the three explosives. Hence, we deduce that the explosive product ions $[M+NO_3]^-$ were mainly produced by the reaction of their molecules M with $[HNO_3+NO_3]^-$, and the probable reason for the improvement of $[M+NO_3]^-$ intensities was that the amount of $[HNO_3+NO_3]^-$ was significantly enhanced after introducing wet air into the WALTP.

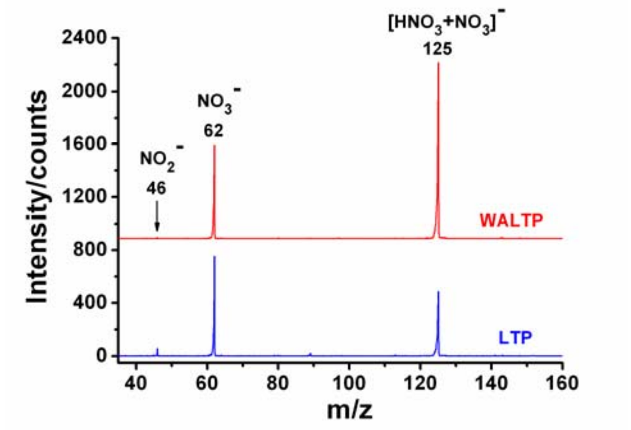

Fig. 3 Mass spectra of reactant ions for the WALTP torch and conventional LTP source, respectively.

The probable enhancement mechanism for [HNO$_3$+NO$_3$]$^-$ in the WALTP was also investigated. In the conventional LTP, the reactant ions were generated just outside the quartz tube. Whereas, in the WALTP, the reactant ions could also be formed inside the quartz tube, in which the concentration of metastable helium atoms was much higher, thus, the amount of reactant ions would be increased. However, except for the improvement of [HNO$_3$+NO$_3$]$^-$ intensity, the intensity of NO$_3^-$ was not changed, and that of NO$_2^-$ was decreased. These unexpected results might be explained as following. The generation processes of NO$_2^-$ and NO$_3^-$ in the WALTP were consistent with those in the atmospheric pressure corona discharge source.[13] After introducing wet air into the plasma stream, the Penning ionization of water molecules by collisions with electronically excited metastable helium atoms could yield an abundance of OH$^·$ radicals (reaction 1), which would rapidly react with NO$_2$ to form neutral HNO$_3$ (reaction 2).[9, 14] Consequently, the intensity of NO$_2^-$ was dramatically reduced, and more [HNO$_3$+NO$_3$]$^-$ would be produced via the association reaction 3.[14b, 15]

$$\mathrm{He}^* + n\mathrm{H_2O} \rightarrow \mathrm{He} + (\mathrm{H_2O})_{n\text{-}1}\mathrm{H}^+ + \mathrm{OH}^· + \mathrm{e} \qquad (1)$$

$$\mathrm{OH}^· + \mathrm{NO_2} + \mathrm{N_2} \rightarrow \mathrm{HNO_3} + \mathrm{N_2} \qquad (2)$$

$$\mathrm{NO_3}^- + \mathrm{HNO_3} + \mathrm{N_2} \rightarrow [\mathrm{HNO_3{+}NO_3}]^- + \mathrm{N_2} \qquad (3)$$

The repeatability of WALTP torch for explosives detection was assessed by measurement of 0.5 ng RDX for 5 times. The relative standard deviation (RSD) was 11.6%, while that using the conventional LTP was 28.5%. The better repeatability of WALTP would make quantitative data more reliable.

The sensitivity of WALTP for the explosives detection was evaluated by the determination of RDX, PETN, and tetryl, respectively. The results suggested that LODs of these explosives were all at the low picogram level, 5, 8, and 15 pg for RDX, tetryl, and PETN respectively, which are much lower than those acquired by the conventional LTP.[6c]

As an application, the WALTP was employed to analyze a mixture consisting of 3 ng RDX, 6 ng PETN, and 6 ng tetryl. The experiment was carried out by the use of WALTP and with its side tube sealed (equal to the conventional LTP[6c]), respectively. As depicted in Fig. 4, it is notable that comparing to those acquired by the conventional LTP, the intensities of [M+NO$_3$]$^-$ for these three explosives are improved. Furthermore, by adopting the WALTP, only one prominent peak [M+NO$_3$]$^-$ for each of the explosives can be obtained, which greatly simplifies the mass spectrum.

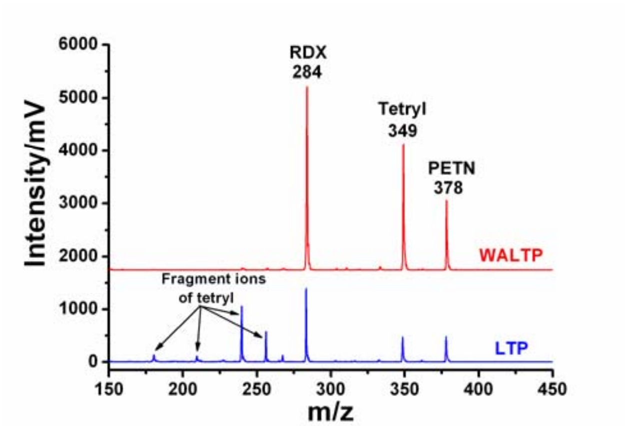

Fig. 4 Mass spectra of a mixture of 3 ng RDX, 6 ng PETN, and 6 ng tetryl obtained by the WALTP torch and with its side tube sealed (equal to the conventional LTP source), respectively.

In summary, a simple, safe, and environment-friendly WALTP torch has been developed and tested for sensitive detection of explosives. Its special configuration basing on a quartz T shaped tube allows wet air to be introduced into the plasma stream via a side tube, which protects the discharge electrodes from corrosion by the oxidizing gas. With the WALTP, the sensitivity and repeatability for the detection of explosives are interestingly improved; and LODs at the low picogram level have been achieved for RDX, PETN, and tetryl (*e.g.*, 5 pg for RDX). The improvement of [M+NO$_3$]$^-$ intensities for the three selected explosives is probably attributed to the increase of reactant ion [HNO$_3$+NO$_3$]$^-$. Finally, the mass spectrum of a mixed explosive sample obtained by the WALTP is characteristic and very clean, which is a benefit for their qualitative and quantitative analysis.

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