Detection of explosives on solid surfaces by thermal desorption and ambient ion/molecule reactions

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Received (in Cambridge, UK) 24th December 2004, Accepted 22nd February 2005
First published as an Advance Article on the web 14th March 2005
DOI: 10.1039/b419291e

A simple, fast and direct method is presented for detecting traces of solid explosives on cotton swabs or in particulate samples: ions are transferred into a mass spectrometer after thermal desorption and corona discharge chemical ionization in ambient air; specificity is enhanced using ambient ion/molecule reactions or by conventional tandem mass spectrometry.

Explosives detection is an important topic[1] for which several mass spectrometric methods have been developed. These include ion mobility[2] and electrospray ionization,[3] secondary electrospray ionization,[4] atmospheric pressure chemical ionization,[5] glow discharge[6] and plasma desorption mass spectrometry.[7] High sensitivity is achieved using halide attachment as a means of generating negatively-charged ions.[5a,b] However, improved performance, including faster detection without extensive sample preparation or pre-concentration, remains highly desirable.

Most explosives are nonvolatile solid compounds with negligible vapor pressure under ambient conditions (*e.g.*, the vapor pressure of RDX at room temperature under 1 atm is *ca.* 5×10^{-9} torr). For this reason, explosives are normally to be found adsorbed on surfaces or on fine particulates in air. This makes the direct detection of explosives under these circumstances challenging. Very recently, two direct mass spectrometric sampling methods have been reported. One is electrospray air sampling,[8] a novel sampling method which uses micro electrospray droplets as "getters". The other is desorption electrospray ionization[9] (DESI) which uses micro electrospray droplets to sample explosives directly from solid surfaces. In a companion study[10] it is shown that DESI gives pg detection limits for explosives on a variety of surfaces in 10 second analysis times.

Herein, we report a direct mass spectrometric method for the detection of surface-adsorbed explosives samples by rapid thermal desorption followed by corona discharge ionization in ambient air. It has long been known[11] that sufficiently rapid heating can be used to transfer unstable molecules into the gas phase before decomposition occurs. This experiment uses this concept but does so in the ambient environment not, as is usually done, in vacuum. The ionization step, which involves ion/molecule reactions used to improve specificity, is also done under ambient conditions[12] and the resulting ions are then transferred into the vacuum environment of the mass spectrometer. This method involves a simple sample handling procedure and has high specificity which can be increased still further by the use of tandem mass spectrometry. The method might be particularly useful for confirmation of positive results of other rapid screening methods such as DESI.[10]

In this study, collected samples of explosives adsorbed on swabs or particulates (fine dust collected from the laboratory) are pyrolysed in an air stream containing chloroform; the gaseous products are then ionized by corona discharge in ambient air and transferred to a mass spectrometer for analysis (Fig. 1). A commercial LCQ ion trap mass spectrometer (Thermo Finnigan, CA) equipped with an atmospheric pressure chemical ionization (APCI) source was employed without modification and operated in the negative ion mode (heated capillary temperature, 100 °C). Note that in principle, any mass spectrometer with an atmospheric interface can be used in this experiment. The chloroform vapor-doped air stream was obtained either by flowing the air over the headspace of a chloroform-containing flask or by nebulizing injected chloroform (10 μL min^{-1}) with an air flow (roughly 10 L min^{-1}).

The swabs (Barringer Technologies Inc., NJ) are those used to wipe luggage for the presence of explosives in airports. The explosive samples were prepared by transferring small volumes of standard solutions (Accoustandards Inc., CT) onto cotton swabs (*ca.* 1.5 cm × 2 cm) or particulates (*ca.* 2 mg). The swabs were placed directly in the heater of the APCI source, rendering the overall method extremely rapid; thermal desorption temperatures for TNT, RDX, and PETN on swabs or particulates were 100, 150 and 150 °C, respectively (the heater temperature can be raised to 400 °C within a few seconds).

As displayed in Fig. 2, characteristic ions are observed for the explosives $[\mathrm{TNT} - \mathrm{H}]^-$ (*m*/*z* 226), $[\mathrm{RDX} + \mathrm{Cl}]^-$ (*m*/*z* 257) and $[\mathrm{PETN} + \mathrm{Cl}]^-$ (*m*/*z* 351). Peaks at *m*/*z* 153, 155 and 157 in Fig. 2 are due to different isotopic forms of $[\mathrm{CHCl_3} + \mathrm{Cl}]^-$. Collision-induced dissociation (CID) of the ion $[\mathrm{TNT} - \mathrm{H}]^-$ (*m*/*z* 226) gives rise to the characteristic fragment of *m*/*z* 196 by loss of NO, consistent with the nitro functionality. The ions of $[\mathrm{RDX} + {}^{35}\mathrm{Cl}]^-$ (*m*/*z* 257) and $[\mathrm{PETN} + {}^{35}\mathrm{Cl}]^-$ (*m*/*z* 351) are characterized by the presence of isotopes $[\mathrm{RDX} + {}^{37}\mathrm{Cl}]^-$ (*m*/*z* 259) and $[\mathrm{PETN} + {}^{37}\mathrm{Cl}]^-$

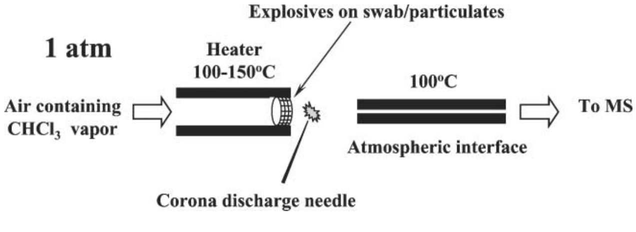

Fig. 1 Thermal desorption/ambient chemical ionization experiment for explosives detection on cotton swabs.

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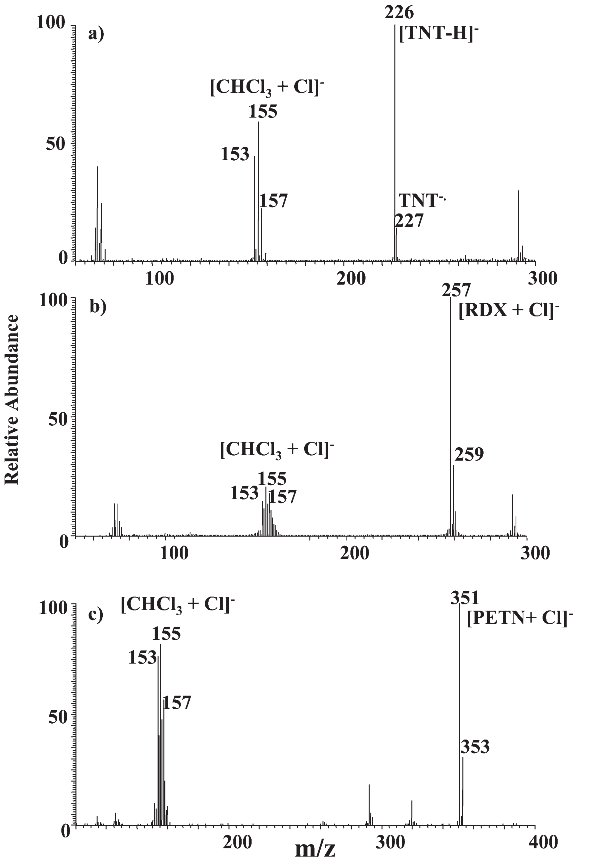

Fig. 2 Mass spectra of: a) TNT (5 μg); b) RDX (10 μg) and c) PETN (2 μg) on cotton swabs during thermal desorption/atmospheric pressure chemical ionization using $CHCl_3$ reagent gas in air.

(*m*/*z* 353), respectively, with one third the abundance. Preliminary results show that the limits of detection (LOD) for this method using single-ion monitoring (SIM) are less than 10 ng (TNT), 30 ng (RDX) and 10 ng (PETN) using a mass spectrometer of modest sensitivity (see Table 1). A pyrolysis-APCI method[13a] used with an APCI-tandem mass spectrometer was reported to have much higher detection limits of formulated compounds such as pharmaceuticals.[13b] The high sensitivity of the present method is probably due to the negative ion detection mode and the short distance (*ca.* 1.5 cm) between the position of explosives samples and the corona discharge needle.

Enhanced selectivity can be achieved using selective ion/molecule reactions[14a] for protection against false positives. The formation of the Meisenheimer complex with a carbanion such as $CH_2NO_2^-$ (see inset in Fig. 3a) is known to be selective to highly electron-deficient aromatic compounds.[14b] In this study the ion/molecule reactions were performed under ambient conditions, which is unusual if not entirely unprecedented.[12] When the air gas stream was doped with nitromethane, the Meisenheimer complex ion $[TNT + CH_2NO_2]^-$ (*m*/*z* 287) was formed from a mixture on a cotton swab of trimethylphenol (MW = 136, 12 μg), camphor (MW = 152, 12 μg), glycyl-leucine (MW = 188, 12 μg), 3-benzyloxybenzaldehyde (MW = 212, 12 μg) and TNT (MW = 227, 4 μg). The CID spectrum of the ion of *m*/*z* 287 shows the formation of a fragment ion of *m*/*z* 226 by loss of nitromethane CH_3NO_2, suggesting that the Meisenheimer complex has been formed (Fig. 3b).[14b] Adducts were not observed for other components of the mixture compounds (Fig. 3a). This clearly demonstrates that this characteristic ion/molecule reaction occurs under atmospheric pressure (presumably occurring in the APCI source) and it demonstrates the enhanced specificity of TNT detection.

Table 1 Explosives analysis results

Explosive	Physical state	Ions observed	LOD	S/N at LOD
TNT	on swab	$[TNT - H]^-$, $TNT^{\cdot -}$	< 10 ng	4 : 1
	on particulate		< 10 ng	3.3 : 1
RDX	on swab	$[RDX + Cl]^-$	< 30 ng	25 : 1
	on particulate		< 30 ng	4 : 1
PETN	on swab	$[PETN + Cl]^-$	< 10 ng	7 : 1
	on particulate		< 10 ng	5 : 1

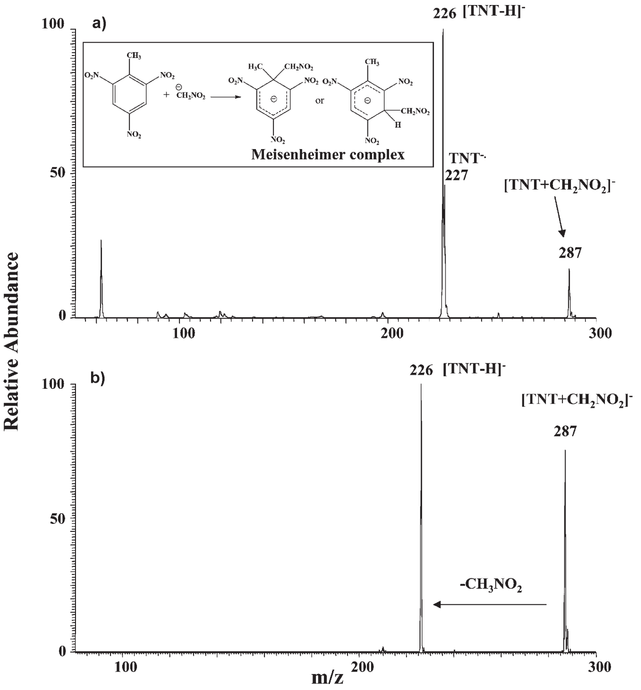

Fig. 3 a) APCI-(−) mass spectrum of TNT in the presence of four other compounds on a cotton swab using nitromethane as the reagent gas. Formation of the Meisenheimer complex $[TNT + CH_2NO_2]^-$ (*m*/*z* 287) increases selectivity for detection of TNT at atmospheric pressure; b) MS/MS product ion of the Meisenheimer complex ion recorded using CID.

In summary, the present method for the detection of explosives on solid surfaces is simple, rapid and sensitive. Due to the specificity obtained from atmospheric pressure ion/molecule reactions and tandem mass spectrometry, it should prove particularly useful for confirmatory tests in airport security monitoring. In particular, it could provide a quick, sensitive response for confirmation of suspected positive results of other rapid screening methods of luggage monitoring, notably DESI.

This work was supported by the National Science Foundation (0412782), the U.S. Civilian Research & Development Foundation (RC1-2493) and the Russian Foundation for Basic Research (RFBR 02-03-32301).

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