

Non-proximate detection of explosives and chemical warfare agent simulants by desorption electrospray ionization mass spectrometry†

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Desorption electrospray ionization (DESI) mass spectrometry is used for the selective and sensitive detection of trace amounts of explosives and chemical warfare agent simulants from ambient surfaces at distances of up to 3 meters from the mass spectrometer.

Explosives and toxic chemicals are widely used to inflict damage on civil populations.^{1–4} Several methods of detecting trace amounts of explosives are currently in use at airports and other transportation facilities^{2,4–8} and there is an interest in exploring alternatives. Desirable qualities in trace explosives detection include high selectivity,^{9,10} so as to avoid false positive and false negative detection; sampling methods that require contact or proximity of the instrumental analyzer and the sample can be slow and inconvenient.^{2,11}

Desorption electrospray ionization (DESI) has recently been shown to have potential value as a trace detection method. It has high selectivity and sensitivity in detecting explosives in trace quantities on contaminated surfaces, even in complex matrices.^{12,13} DESI is based on directing a pneumatically-assisted electrospray of a solvent onto a surface bearing a sample of interest, and then collecting the ions generated by the interaction of the charged microdroplets with the neutral molecules of the analyte present on the surface.¹²

In this Communication, we demonstrate DESI to be a selective and sensitive method for the rapid, non-proximate detection of trace amounts of explosives and CWA simulants from ambient surfaces at distances of up to 3 meters from the mass spectrometer (MS). These demonstration experiments use a rudimentary non-proximate detection device. We also demonstrate increased selectivity by reactive-DESI¹² experiments employing solvent additives, which bind to explosives to form characteristic adduct ions and also by tandem mass spectrometry (tandem MS). Remarkably, the non-proximate spectra are of high quality and largely free of background interference even though signal levels are low. Mass spectra of various explosives (RDX, HMX, PETN, TNT, Composition C4, and TATP) and a CWA simulant (DMMP) were recorded by using methanol/water (70 : 30) as spray solvent doped with sodium chloride (10 mM NaCl) or trifluoroacetic acid (10 mM TFA) in order to enhance the selectivity and instrumental response by forming stable adducts with the explosives or DMMP. (Sample analysis and preparation details are provided in Supporting Information.)

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Limits of detection (LOD) for all explosives at 1 and 3 meters from the mass spectrometer are summarized in Table 1. Note that LOD refers to the total amount of analyte present on the surface and to a 3 : 1 signal-to-noise (S/N) ratio. Samples of explosives were deposited on such surfaces as paper, laptop computers and metal, in an area of 1 cm², of which some 4 mm² was typically sampled.¹²

To investigate whether ions can survive transport over long distances to the mass spectrometer, a DESI source was adapted to sample ions at distances up to 3 meters. In non-proximate detection by DESI, the mass spectrometer and the DESI source are physically separated, but connected by a long stainless steel ion transport tube (1.8 mm ID, 3.18 mm OD), which allows the collection/transport of ions through air back to the mass spectrometer after they leave the surface. This still crude arrangement decreases the losses expected for an open environment (Fig. 1).

Ion transport through air is assisted by the vacuum of the mass spectrometer. The transport tube has a control arm that allows movement of the DESI source across the surface as needed in order to raster the entire surface looking for explosives. The N₂ supply line and the solvent spray inner capillary for the DESI source are conveniently routed along the length of the transport tube. The solvent was sprayed at a flow rate of 3 μl/min with an applied high voltage of 5 kV.

Fig. 2a shows the negative ion DESI spectrum of 1 ng of RDX deposited in an area of 1 cm² on a laptop computer with the DESI spray tip placed 2 mm from the mass spectrometer (typical of DESI experiments). Significant adduct ions occur at *m/z* 479, *m/z* 481, *m/z* 257, *m/z* 259, *m/z* 297 and *m/z* 331; they correspond to [2RDX + ³⁵Cl][−], [2RDX + ³⁷Cl][−], [RDX + ³⁵Cl][−], [RDX + ³⁷Cl][−], [RDX + C₃H₇O₂][−], the RDX adduct of the hemiacetal anion at *m/z* 75 [C₃H₇O₂][−],¹² and the chloride adduct of the HMX impurity^{14,15} [HMX + ³⁵Cl][−], all as confirmed by tandem MS.

Table 1 Explosives analysis by non-proximate DESI-MS^a

Explosive	+/−	Ion observed	LOD at 1 meter	LOD at 3 meter
TNT	−	TNT [−]	1 ng ^b	10 ng ^b
RDX	−	(RDX + Cl) [−]	1 ng ^b	5 ng ^b
		(RDX + Cl) [−]	0.5 ng ^d	4 ng ^d
		(RDX + TFA) [−]	1 ng ^b	5 ng ^b
HMX	−	(HMX + Cl) [−]	1 ng ^b	5 ng ^b
		(PETN + Cl) [−]	10 ng ^b	20 ng ^b
PETN	−	(PETN + Cl) [−]	10 ng ^b	20 ng ^b
TATP	+	(TATP + Na) ⁺	1 ng ^b	10 ng ^b
C4	−	(RDX + Cl) [−]	1 ng ^b	5 ng ^b
DMMP	+	(2DMMP + Na) ⁺	0.5 ng ^d	3 ng ^d
		(2DMMP + Na) ⁺	1 ng ^c	5 ng ^c
		(2DMMP + Na) ⁺	1 ng ^b	4 ng ^b

^a Data cover a number of different surfaces for each explosive and CWA, including ^b plastic (laptop computers), ^c metal and ^d paper.

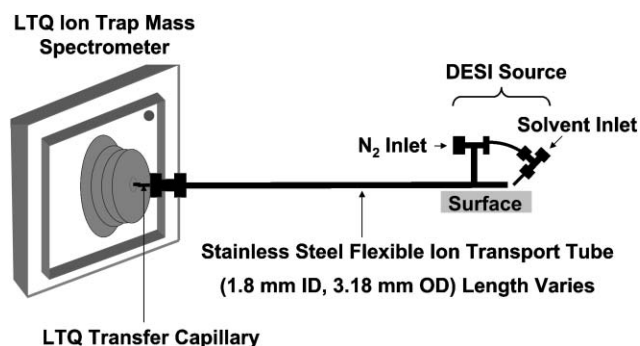


Fig. 1 Non-proximate apparatus used to screen for explosives up to 3 meters from the mass spectrometer.

Data were obtained using sample to mass spectrometer distances of 1 m (Fig. 2b) and 3 m (Fig. 2c) by changing the length of the ion transport tube (see Fig. 1).

At 1 meter, the most significant ions observed in the mass spectrum are RDX adducts with chloride (Cl^-) ions which appear at m/z 479 [$2\text{RDX} + {}^{35}\text{Cl}$] $^-$, m/z 481 [$2\text{RDX} + {}^{37}\text{Cl}$] $^-$, m/z 257 [$\text{RDX} + {}^{35}\text{Cl}$] $^-$, m/z 259 [$\text{RDX} + {}^{37}\text{Cl}$] $^-$, m/z 331 [$\text{HMX} + {}^{35}\text{Cl}$] $^-$, and the RDX adduct with nitrate at m/z 284 [$\text{RDX} + \text{NO}_3$] $^-$ as confirmed by tandem MS. The adventitious nitrate could arise from the water used in the spray solvent or from the environment. All these adduct ions survive transfer through the tube into the mass spectrometer, showing a high relative probability for survival, probably because of the high affinity of these simple ions for RDX. At 1 meter (Fig. 2b), the absolute intensity of the base peak at m/z 257 [$\text{RDX} + {}^{35}\text{Cl}$] $^-$ decreased by two orders of magnitude as compared to the absolute intensity recorded at 2 mm from the mass spectrometer (Fig. 2a). This is most likely due to reactive collisions of the ions in the transport tube on their way from the

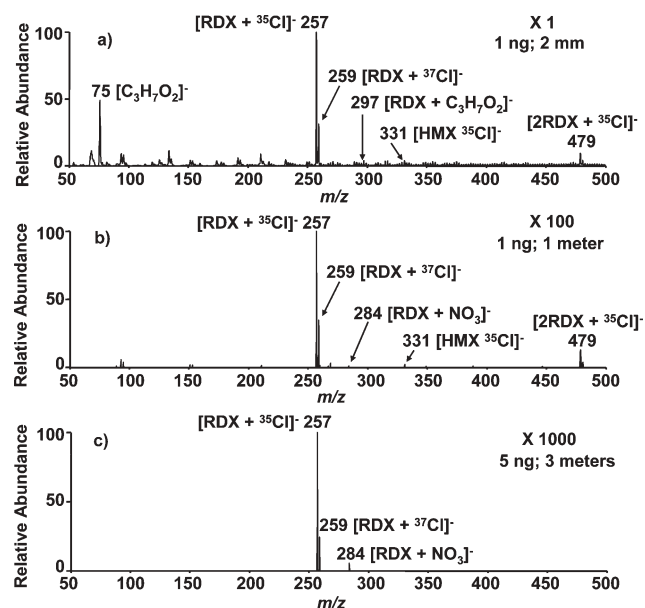


Fig. 2 (a) Negative ion DESI spectrum of 1 ng RDX deposited on 1 cm^2 of the surface of a laptop computer placed at a distance of 2 mm from the mass spectrometer. Methanol/water/NaCl (70 : 30 : 10 mM) was used as the spray solvent. (b) The same experiment at 1 meter. (c) Negative ion DESI spectrum of 5 ng RDX deposited on 1 cm^2 of a laptop computer 3 meters from the mass spectrometer.

surface back to the mass spectrometer. Collisional loss of analyte ions is offset by the proportionately greater loss of background ions from the RDX mass spectrum, resulting in improved S/N characteristics for the RDX ions.

Fig. 2c shows the most significant adduct ions at a distance of 3 meters from the mass spectrometer in the negative ion DESI spectrum of 5 ng RDX, deposited in an area of 1 cm^2 on a laptop computer. Under these conditions, only RDX adducts with chloride and nitrate ions are observed in the spectrum; they fall at m/z 257 [$\text{RDX} + {}^{35}\text{Cl}$] $^-$, m/z 259 [$\text{RDX} + {}^{37}\text{Cl}$] $^-$ and m/z 284 [$\text{RDX} + \text{NO}_3$] $^-$. The data show remarkably good S/N characteristics due to the strong affinities of chloride and nitrate ions for RDX. Peak assignments were confirmed by tandem MS. Contrasting the spectrum recorded at 1 m (Fig. 2b) with that obtained at 3 meters, the greater distance results in a further order of magnitude decrease in signal intensity for the ion at m/z 257 [$\text{RDX} + {}^{35}\text{Cl}$] $^-$, for a total of three orders of magnitude less signal as compared to the typical DESI distance of 2 mm (Fig. 2a). The order of magnitude decrease in signal, when compared to the 1 meter experiment, is offset by the even greater decrease in the background signal giving an essentially noise-free spectrum. The remarkable drop in background (chemical noise) seen especially at greater distances is not completely understood; the 3 m spectrum in the negative ion mode is especially remarkable for lack of all signal except that due to the analyte.

The same experiment was performed using methanol as the spray solvent, both with and without water (data not shown). When pure methanol was sprayed onto the surface, no ions corresponding to RDX were observed. This contrasts with the results obtained by using pure water as spray solvent, which showed results similar to those previously observed for the NaCl containing aqueous methanol solution, including typical RDX adducts with chloride ions at m/z 479 [$2\text{RDX} + {}^{35}\text{Cl}$] $^-$, m/z 481 [$2\text{RDX} + {}^{37}\text{Cl}$] $^-$, m/z 257 [$\text{RDX} + {}^{35}\text{Cl}$] $^-$, and m/z 259 [$\text{RDX} + {}^{37}\text{Cl}$] $^-$. The source of chloride is probably the water used in the solvent spray and/or the laptop surface. Use of pure water as a spray is useful when there are safety concerns with the use of methanol as the spray solvent.

In a separate experiment, the spray solvent (methanol/water, 70 : 30) was doped with sodium chloride and trifluoroacetic acid (TFA) (10 mM each) and sprayed onto the surface of a laptop computer. The surface had been treated with 1 ng of RDX and this choice of spray solution was made in order to examine the selective detection of RDX by forming stable adducts with multiple dopants (Fig. 3). The TFA anion [$\text{TFA} - \text{H}$] $^-$ is observed at m/z 113 and it forms a stable adduct with RDX which appears at m/z 335 (Fig. 3). The adduct ion at m/z 335 undergoes collision induced dissociation (CID) giving rise to deprotonated TFA at m/z 113 by loss of an RDX molecule.

Ions at m/z 257, m/z 259, m/z 479, and m/z 481 correspond to the previously seen chloride adducts with RDX, as confirmed by tandem MS. The LOD obtained for RDX using TFA and NaCl as the reactive additives was 1 ng. RDX adducts with [$\text{TFA} - \text{H}$] $^-$ and Cl^- anions show remarkably good S/N characteristics (Fig. 3). This reactive-DESI approach, in combination with tandem MS, provides another tool to help confirm the presence and identity of RDX, especially in complex matrices.

The plastic explosive, Composition C4, was analyzed by DESI using a sample to spectrometer distance of 3 meters. Fig. 4 shows

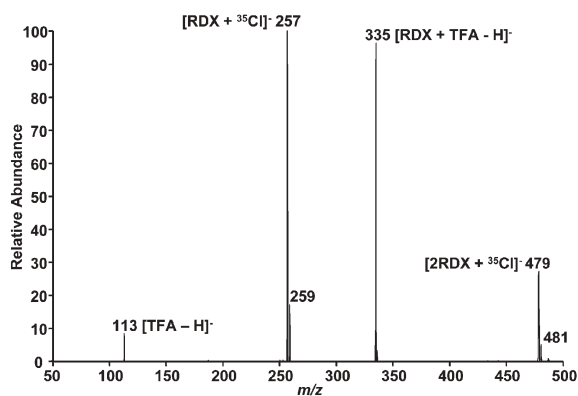


Fig. 3 Negative ion DESI spectrum of 1 ng RDX deposited on 1 cm² of a laptop computer at a distance of 1 meter from the mass spectrometer. Methanol/water/NaCl/TFA (70 : 30 : 10 mM : 10 mM) was the spray solvent.

the most significant adducts ions in the negative ion DESI spectrum of 10 ng C4, deposited in an area of 1 cm² on a laptop computer. Adducts occur at m/z 479 [2RDX + ³⁵Cl]⁻, m/z 481 [2RDX + ³⁷Cl]⁻, m/z 257 [RDX + ³⁵Cl]⁻, m/z 259 [RDX + ³⁷Cl]⁻, and m/z 331 [HMX + ³⁵Cl]⁻. Peak assignments were confirmed by tandem MS, as illustrated in the inset of Fig. 4 for the ion at m/z 479 [2RDX + ³⁵Cl]⁻ which fragments by losing an RDX molecule to give a product ion at m/z 257 [RDX + ³⁵Cl]⁻.

In a similar set of experiments, DMMP was detected in the positive ion mode by its adducts with Na⁺ ions at m/z 147 [DMMP + Na]⁺ and m/z 271 [2DMMP + Na]⁺ using an aqueous NaCl spray solution. Tandem mass spectrometry was used to confirm peak identities. These ions were the most significant species in the mass spectrum recorded at a distance of 1 meter from the mass spectrometer, while at 3 meters, the ion at m/z 271 [2DMMP + Na]⁺ was the only species observed in the mass spectrum. (For information on experimental procedures, performance and spectra, refer to Supporting Information.)

Throughout this set of experiments, highly favored ion-molecule adducts¹⁶ were observed; the apparent high affinities of the explosives for the available anions resulted in stable complexes

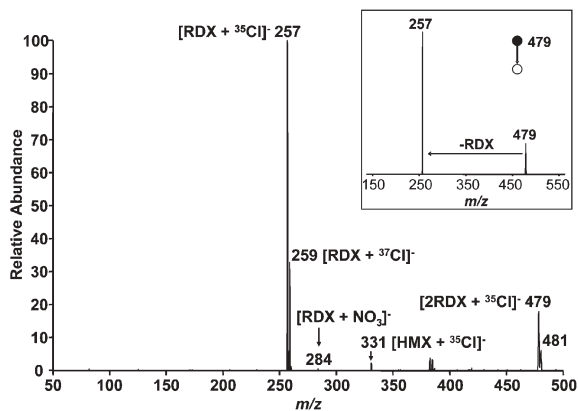


Fig. 4 Negative ion DESI spectrum of 10 ng Composition C4 deposited on 1 cm² of a laptop computer and examined using a surface to mass spectrometer distance of 3 meters. Methanol/water/NaCl (70 : 30 : 10 mM) was used as the spray solvent. The inset shows the MS/MS spectrum of the ion of m/z 479.

which remain intact during passage through the ion transport system. The distance-dependent phenomenon observed here is analogous to the time-dependent behavior typically observed in atmospheric pressure chemical ionization (APCI), where thermodynamically stable ions come to dominate the mass spectra at long times. In APCI, as here, the spectra contain nucleophilic adducts of the analyte formed *via* chloride ion-molecule association reactions.^{16–18} An efficient way to screen out interferences from complex matrices is therefore to add into the spray solvent a dopant that has a high affinity for the analyte of interest. This gives high sensitivities and S/N ratios in these experiments performed at atmospheric pressure and temperature.

The non-proximate detection experiments reported here may expand the uses of mass spectrometry by increasing its capabilities and flexibility. Traditionally, the sample had to be collected and then ionized in the mass spectrometer, even in the case of gaseous samples which are easily transported to the mass spectrometer for analysis. The recent development of ambient ionization methods such as DESI¹⁹ lifted the sample preparation restriction but continued to require spatial proximity of the sample and mass spectrometer. With the present approach, the sample is ionized at the sampling site and the resulting ions are transported directly and continuously into the instrument for analysis.

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