Accelerated Articles

Desorption Electrospray Ionization of Explosives on Surfaces: Sensitivity and Selectivity Enhancement by Reactive Desorption Electrospray Ionization

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Desorption electrospray ionization (DESI), an ambient mass spectrometry technique, is used for trace detection of the explosives trinitrohexahydro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 2,4,6-trinitrotoluene (TNT), Pentaerythritol tetranitrate (PETN), and their plastic compositions (Composition C-4, Semtex-H, Detasheet) directly from a wide variety of surfaces (metal, plastic, paper, polymer) without sample preparation or pretreatment. Analysis of the explosives is performed under ambient conditions from virtually any surface in very short times (<5 s) including confirmatory tandem mass spectrometry (MS/MS) experiments, while retaining the sensitivity and specificity that mass spectrometry offers. Increased selectivity is obtained both by MS/MS and by performing additional experiments in which additives are included in the spray solvent. These reactive DESI experiments (reactions accompanying desorption) produce such ions as the chloride and trifluoroacetate adducts of RDX and HMX or the Meisenheimer complex of TNT. Desorption atmospheric pressure chemical ionization, a variant of DESI that uses gas-phase ions generated by atmospheric pressure corona discharges of toluene or other organic compounds, provides evidence for a heterogeneous-phase (gaseous ion/absorbed analyte) charge-transfer mechanism of DESI ionization in the case of explosives. Plastic explosives on surfaces were analyzed directly as fingerprints, without sample preparation, to test DESI as a possible method for in situ detection of explosives-contaminated surfaces. DESI also allowed detection of explosives in complex matrixes, including lubricants, household cleaners, vinegar, and diesel fuel. Absolute limits of detection for the neat explosives were subnanogram in all cases and subpicogram in the case of TNT. The DESI response was linear over 3 orders of magnitude for TNT. Quantification of RDX on paper gave a precision (RSD) of 2.3%. Pure water could be used as the spray solution for DESI, and it showed ionization efficiencies for RDX in the negative ion mode similar to that given by methanol/water. DESI represents a simple and rapid way to detect explosives in situ with high sensitivity and specificity and is especially useful when they are present in complex mixtures or in trace amounts on ordinary environmental surfaces.

The development of highly sensitive techniques capable of trace-level detection and unequivocal identification of analytes is increasingly desirable in analytical chemistry. There is a strong demand for methods for the field analysis of involatile and thermally unstable compounds with rapid response times, preferably without special sample preparation. No general methods are currently available that meet these criteria.

Appropriate techniques would be capable of high-throughput analysis with very fast responses, preferably in less than 10 s. Important applications for such technologies include public safety monitoring,[1] forensic applications,[2] and environmental analysis.[3,4] The extremely low vapor pressures of some explosives, the limited

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sample sizes, deliberate concealment, and their co-occurrence with interfering compounds make trace and residue explosives analysis a difficult task.[5] In situ analysis of explosives particles from contaminated surfaces without sample handling or preparation is desirable to avoid sample loss or cross-contamination associated with sample manipulation.

A wide variety of detection methods and sampling techniques have already been developed and used to detect and analyze explosives under various sampling conditions.[6] Vapor and particle detection systems are in continuous worldwide use to detect bulk and trace quantities of explosives via their unique characteristics in their elemental spectra.[2] Ion mobility spectrometry (IMS),[7–12] a common trace detection method, is used at checkpoints in airports around the world. Some attributes of this technique are ionization at atmospheric pressure, low detection limits, very high sensitivity, portability, and rapid analysis.[13,14] Despite these advantages, IMS suffers from disadvantages that include nonlinear response, poor selectivity, and difficulties in the identification and quantification of analytes present in complex mixtures due to interactions between the reagent gas and the matrix.[13]

Mass spectrometry (MS) is more informative than IMS in terms of identifying organic compounds in trace amounts.[6] It combines high sensitivity with the best specificity of any general technique applicable to explosives analysis. Mass spectrometry also offers other advantages such as short response times, as well as the additional selectivity available from MS/MS experiments and ion/molecule reactions.[15–18] Despite these advantages, mass spectrometry has limitations including inconvenient size, cost, and complexity, and in the past, mass spectrometric analysis has often required significant sample preparation. Explosives present special problems for both IMS and MS due to their great range of volatilities while their occurrence on surfaces makes their direct ionization difficult by traditional methods.

The high electron affinities associated with the nitro or nitrate functional groups present in the overwhelming majority of explosives in common use mean that they readily form negative ions by electron capture. This has been taken advantage of in corona discharge,[19] glow discharge,[20,21] and electrospray ionization

(ESI)[22] methods that have been used for the analysis of explosives using the negative ion mode.

ESI is widely used to ionize organic compounds including explosives in solution.[6,10,22–24] In some experiments adducts are deliberately formed with additives in the electrospray solvent such as chloride, nitrite, trifluoroacetate (TFA), formate, acetate, and nitrate.[9,23,25,26] This results in increased sensitivity and specificity for explosives analysis.[9] While this technique is useful for the ionization and analysis of explosives, solid samples must be transferred into solution for analysis.

Various desorption/ionization methods are applicable to the analysis of solids on surfaces.[27] In those few cases in which the sample is not examined under vacuum, atmospheric pressure matrix-assisted laser desorption/ionization[28,29] and atmospheric pressure photon ionization,[30] the sample is not accessible during analysis; i.e., the experiment is not done in the ordinary ambient environment and the sample cannot be manipulated by ordinary physical or chemical means. Since in situ detection has not been possible previously, the approach usually pursued involves wiping the ambient surface with a special cloth material followed by thermal desorption/gas-phase ionization of the explosives compounds from that cloth.[5,13,31–33] This dry sampling/thermal desorption method is sufficiently successful to be used as the standard sampling technique at airports. Nevertheless, it is limited by the need for manual sample transfer, by the fact that it is relatively slow, and because it is not ideal for the detection of thermally labile explosives or explosives that have extremely low vapor pressures.[34]

In a preliminary communication, we reported the use of the new ambient sampling technique of desorption electrospray ionization (DESI)[35] for the detection of trace amounts of explosives on a variety of ambient surfaces without any sample preparation.[36] The DESI ionization technique is based on directing a pneumatically assisted electrospray onto a surface and collecting the secondary ions generated by the interaction of charged microdroplets or gas-phase ions derived from the electrospray with neutral molecules of analyte present on the surface.[35,36] In the original communication, a variant on DESI called desorption

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atmospheric pressure chemical ionization (DAPCI)[36] was also reported as a method to investigate explosives and to characterize the DESI ionization mechanism. Instead of using a liquid as solvent spray, gaseous solvent vapor is ionized by corona discharge in this alternative procedure, and the resulting plasma is used to create ions of the explosives directly from the surface of interest. Recently, another ambient ionization method, direct analysis in real time (DART), was reported.[37] In DART, an electrical discharge in a gas (in this case nitrogen or helium) is used to produce ions, electrons, and excited-state atoms in a plasma.[37] Penning ionization by metastable atoms is reported to be responsible for desorption and ionization of the analyte.

In the present paper, we expand greatly on our previous study.[35] We use DESI as a sensitive and selective ionization method for detecting trace amounts of explosives and apply it to plastic explosives compositions in a variety of complex matrixes and to the use of ion/molecule reactions in order to increase selectivity. The explosives studied, trinitrohexahydro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 2,4,6-trinitrotoluene (TNT), Pentaerythritol tetranitrate (PETN) and the plastic compositions, Composition C-4, Semtex-H, and Detasheet, were analyzed in situ under ambient conditions from common surfaces without sample pretreatment. These are the main advantages that the DESI method offers compared to other desorption/ionization methods with the exception of DART, which is also an ambient method and which may have a performance similar to DESI (at least for compounds of low molecular weight) although this remains to be established. Increased selectivity in DESI is derived from the fact that mass spectra can be recorded in both the positive and the negative ion modes, and by the availability of MS/MS experiments and reactive DESI experiments that employ solvent additives that bind to the explosives to form characteristics adduct ions. Fingerprints of plastic explosives were detected directly on several surfaces without sample preparation. As is shown in this study, DESI retains the advantages of sensitivity and specificity that characterize mass spectrometry and combines these with very short (<5 s) total analysis times, no sample preparation/pretreatment at all, and the ability to detect explosives in situ on virtually any surface at ultratrace levels.

EXPERIMENTAL METHODS

Chemicals and Reagents. TFA, acetaldehyde-d_4, methanol-d_4, and 2-propanol were purchased from Sigma-Aldrich (Milwaukee, WI). Hydrochloric acid and methanol (HPLC grade) were purchased from Mallinckrodt Baker Inc. (Phillipsburg, NJ). Deionized/distilled water was obtained from a Barnstead/Thermolyne deionizer unit (Barnstead Mega-Pure System) (Dubuque, IA). RDX, HMX, and TNT standards were purchased as 1 mg/mL solutions in methanol/acetonitrile (1:1) from AccuStandard Inc. (New Haven, CT), and PETN was purchased as a 0.1 mg/mL solution in methanol from the same supplier. Sodium methoxide used to form the Meisenheimer complex was purchased from Sigma-Aldrich. Toluene for the DAPCI experiments was purchased from Sigma-Aldrich. Plastic explosives compositions were obtained as solutions of 1000 ng/mL in methanol from the Federal Aviation Administration (FAA) trace detection program

(William J. Hughes Technical Center, Atlantic City, NJ). The compositions of these solutions are based on information provided by the FAA regarding the primary explosive content (RDX or PETN) in the plastic compositions. The exact composition and concentrations in these solutions other than the primary explosive components (RDX or PETN) were not specified by the FAA. Fingerprints of Composition C-4 were obtained on glass slides from the FAA trace detection program (William J. Hughes Technical Center).

Sample and Electrospray Solvent Preparation. Each compound was diluted in methanol (HPLC grade) to the desired concentration. From each solution, 10 μL was deposited using a pipet (Brinkmann, Westbury, NJ) onto a 1-cm^2 total surface area, unless otherwise specified, and then allowed to dry prior to analysis. The spray solvent was usually a methanol/water (1:1) mixture, sometimes doped to a concentration of 0.05% TFA or HCl as indicated. For Meisenheimer complex formation, a 10 ppm sodium methoxide solution in methanol was used as the electrospray solvent.

Fingerprint Impressions and Transfers on Glass Slides. Impressions were made by placing the thumb in direct contact with the plastic explosive (Composition C-4) for a predetermined amount of time. Then the contaminated finger was used to impress the Composition C-4 fingerprint onto a glass slide surface. For transfer experiments, the thumb was placed in direct contact with the previously made fingerprint impressed on the glass slide and then used to impress (transfer) a second fingerprint onto a second glass slide. This procedure was repeated for up to five transfers.

DESI and DAPCI Ion Sources. Experiments employed an early prototype DESI source (OmniSpray Source, Prosolia, Inc., Indianapolis, IN) consisting of an inner spray capillary (0.10-mm i.d., 0.15-mm o.d.) and an outer gas nebulizer made of a deactivated fused-silica capillary (0.25-mm i.d., 0.40-mm o.d.) from Agilent Technologies (Wilmington, DE). The DESI source was mounted on an x,y,z-moving stage, allowing it to be positioned at any chosen point with respect to the sample. The moving stage also has a tangent arm drive miniature stage that allows precise angular adjustment from 0 to 90° (Figure 1). Nitrogen is used as the nebulizing gas at a linear velocity set to 350 m/s. The solvent was sprayed at a flow rate of 3 μL/min, under the influence of an applied high voltage that was typically in the range 3−6 kV. The gas jet was composed of electrosprayed aqueous microdroplets, and free gas-phase ions were directed onto the surface at an incident angle of 35° to the normal. The projectile droplets, ions, and neutrals desorb analyte ions at a shallow angle from the surface. These are transferred as a result of electrostatic and pneumatic forces to a mass spectrometer equipped with an atmospheric pressure ion-transfer line. The distance from the spray source tip to sample was 1 mm, giving a sampling area of just 4 mm^2, a small fraction of the total 1-cm^2 area onto which the sample was deposited.

The main difference between DESI and DAPCI is the substitution of the spray solvent used in DESI to generate the reactant ions by a gaseous solvent vapor (methanol, toluene) in DAPCI. The solvent vapor was ionized by a corona discharge formed by applying a high voltage, typically 3−6 kV, to a tapered tip stainless steel needle that replaces the electrospray emitter used in DESI. The discharge ionizes vapors of the volatile reagent (water,

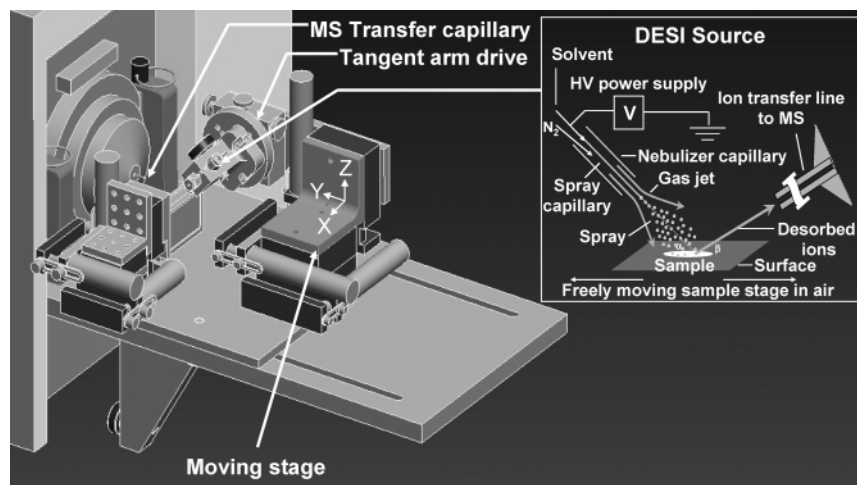(37) Cody, R. B.; Laramee, J. A.; Durst, H. D. *Anal. Chem.* **2005**, *77*, 2297−2302.

Figure 1. DESI source and moving stage used to position the source; an early prototype of the OmniSpray source of Prosolia, Inc. The source is fitted with a short (1 cm) ion-transfer capillary.

MeOH, toluene, etc.), which flows coaxially to the nebulizing nitrogen gas used to transfer the ions to the surface.

Mass Analyzer, Data Processing, and DESI/DAPCI Source Conditions. Experiments were performed using a commercial linear ion trap (Finnigan LTQ, Thermo Electron Corp., San Jose, CA). Data were processed using the instrument software interface (Xcalibur version 1.4 SR1). DESI conditions used in both the positive and negative ion modes were as follows: source voltage (applied to the spray capillary), 5 kV; tube lens voltage, ± 65 V; capillary temperature, 150 °C; heated capillary voltage, ± 15 V; multipole rf amplitude (V_{p-p}), 400 V; and multiplier voltages 1 and 2, -800 V. The ion injection time was set to 100 ms, and the number of microscans was set to three. A total spectral acquisition time of 3 s was used.

DAPCI source conditions used for RDX analysis in the positive ion mode were as follows: source voltage (applied to the tapered tip stainless steel needle), 4 kV; tube lens voltage, 78 (methanol) and 207 V (toluene); capillary temperature, 150 °C; heated capillary voltage, 19 (methanol) and 40 V (toluene); multipole rf amplitude (V_{p-p}), 400 V; multiplier voltages 1 and 2, -800 V; ion injection time, 100 ms; and number of microscans, three. The conditions used for TNT analysis using DAPCI in the negative ion mode were as follows: source voltage (applied to the tapered tip stainless steel needle), 4 kV; tube lens voltage, -102 V; capillary temperature, 150 °C; heated capillary voltage, -20 V; multipole rf amplitude (V_{p-p}), 400 V; multiplier voltages 1 and 2, -800 V; ion injection time, 100 ms; and number of microscans, three.

RESULTS AND DISCUSSION

The organization of the paper is as follows. First, positive ionization of RDX is discussed to introduce the data for this key explosive. This is followed by a section on negative ionization and reactive DESI, which presents data for RDX as well as other explosives. In the reactive DESI experiment, ion/molecule reactions are performed at the sample surface in atmosphere and these adducts are used for confirmatory identification of explosives constituents. The next section deals with a variety of aspects of analytical performance, including quantitation. It in turn is followed by discussion of the related DAPCI method and the implications of the DAPCI data for the DESI mechanism. Finally, we discuss plastic explosives and more complex mixtures.
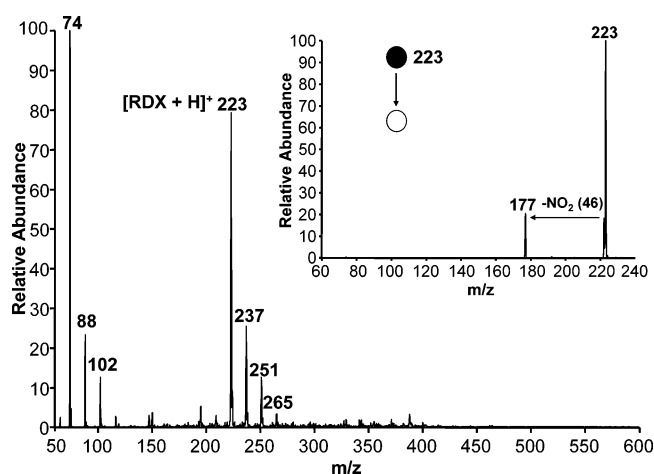
Figure 2. Positive ion DESI spectrum of 10-pg total amount of RDX deposited on paper in an area of 1 cm². Methanol/water (1:1) was used as the spray solvent. The presence of the explosive is confirmed by the product ion MS/MS spectrum of protonated RDX (inset).

Positive Ion DESI experiments. *RDX Positive Ion Mode.* The positive ion DESI mass spectrum of RDX, using 10 pg on a 1-cm² spot on paper, was recorded using methanol/water (1:1) as the spray solvent. The peak at m/z 223 (Figure 2) corresponds to protonated RDX, $(M+H)^+$. The inset in Figure 2 shows the product ion scan MS/MS spectrum of this ion, m/z 223, which loses a nitro group as a result of homolytic cleavage of the low-energy $N-NO_2$ bond.[38] The high proton affinity of RDX allows for its protonation by methanol/water. An interesting feature of the positive ion spectrum of RDX is that the related nitramine HMX does not show the same type of ionization under similar experimental conditions, even using much greater amounts (ng range) of analyte. This observation is most likely due to its lower proton affinity. Other ions occur at mass/charge increments of 14 (m/z 237, 251, 265) and are tentatively assigned as (RDX + CH_3)$^+$, (RDX + C_2H_5)$^+$, and (RDX + C_3H_7)$^+$. The explosive RDX showed a limit of detection (LOD) of 1 pg with a S/N ratio of 4:1 when analyzed from paper. The analytical performance of the DESI technique in the positive ion mode was evaluated over the

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range of absolute amounts from 1 to 100 pg and showed good reproducibility (relative standard deviation, RSD < 3% for 1-pg samples deposited on 1 cm^2 of paper). The DESI response was linear over the range 1–10 pg ($y = 146.63x + 1138.9$ with an R^2 value of 0.9978), but after this point saturation of the response began.

Negative Ion DESI experiments. *TNT and PETN Detection in the Negative Ion Mode.* As is well known, the nitro or nitrate functional groups contained in explosives have high electron affinities, allowing for the formation of negative ions by electron capture.[23,24] TNT could be detected after 10 fg (total amount) had been deposited on a 1-cm^2 area. This highly demanding criterion was met for all surfaces sampled (glass, paper, plastic, floppy disk, hard drive, metal, swab, nitrile gloves). Two ions observed for all these surfaces, m/z 197 and 227, correspond to the radical anion of TNT$^{\cdot-}$ and to the fragment formed by loss of NO, respectively, as corroborated by tandem MS. These ions were previously observed in the mass spectrum of TNT by using ESI,[22] negative chemical ionization,[39] and atmospheric pressure chemical ionization (APCI).[40] Collision-induced dissociation (CID) of the ion m/z 227 shows characteristic fragment ions corresponding to (TNT − OH)$^-$, (TNT − NO)$^-$, and (TNT − NO$_3$)$^-$.

PETN, a nitrate ester, was analyzed by DESI using the negative ion mode; 100 pg total deposited on paper in an area of 1 cm^2 represents the detection limit for this explosive. The ions at m/z 315, 351, and 353 observed in the DESI mass spectrum of PETN are attributed to (PETN − H)$^-$ and to the ^{35}Cl and ^{37}Cl isotopic peaks of (PETN + Cl)$^-$; all these ions have been observed previously in the ESI spectrum.[22]

RDX Detection in the Negative Ion Mode Using Chloride Attachment. In addition to exploiting the formation of negative ions by electron capture[23,24] the instrument response for explosives was enhanced by the use of additives that form stable adducts. Previous experiments using ESI and APCI showed that chloride (from either NH$_4$Cl or NaCl) and TFA form very stable adducts ions with RDX and HMX.[22,25,40] Negative ion DESI similarly allows the formation of very stable adducts while producing few fragments, making it a very gentle method for explosives analysis. Figure 3 shows the DESI mass spectrum of a 1-ng RDX sample deposited on paper in an area of 1 cm^2. As in the other experiments, only a small fraction of the sample was interrogated. Good reproducibility was obtained (RSD < 3% at a level of 1 pg on paper in a total area of 1 cm^2) for RDX in the negative ion mode. The spray solution composed of methanol/water (1:1) was doped with HCl to a final concentration of 0.05% HCl. Note that the characteristic RDX adducts[23] were barely seen without the addition of the chloride additive.

The most significant adducts ions in the negative ion DESI spectrum of 1 ng of RDX, deposited in an area of 1 cm^2, occur at m/z 519, 479, 481, 297, 257, and 259 and correspond to (2RDX + 75)$^-$, (2RDX + ^{35}Cl)$^-$, (2RDX + ^{37}Cl)$^-$, (RDX + 75)$^-$, (RDX + ^{35}Cl)$^-$ and (RDX + ^{37}Cl)$^-$, respectively, assignments that were confirmed using tandem MS (Figure 3). Tandem MS improved the limits of detection and specificity, and this is especially valuable in the analysis of complex mixtures. The chloride adduct (RDX + Cl)$^-$ gave the most abundant ions in the negative ion
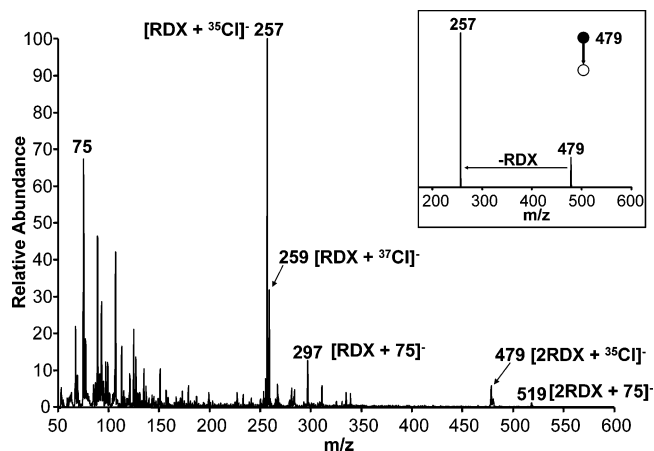
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Figure 3. Negative ion DESI mass spectrum of 1 ng of RDX total amount deposited on 1 cm^2 of paper. Methanol/water/HCl (1:1:0.05%) was used as the spray solvent. The inset shows the MS/MS spectrum of m/z 479.

DESI mass spectrum for RDX, allowing for ready identification of RDX by using the isotopic signature and tandem MS. The ion at m/z 519 fragments under CID conditions to give a product ion at m/z 297 (RDX + 75)$^-$ by loss of an RDX molecule. The ion at m/z 297 fragments further to give a product ion at m/z 221 corresponding to the RDX anion. For the ion at m/z 479, fragmentation under CID conditions occurs by loss of one RDX molecule to give a product ion at m/z 257 (RDX + ^{35}Cl)$^-$. The use of dopants in the spray solvent to produce selective ion/molecule reaction products, when used in combination with tandem MS, provides the selectivity needed to confirm the presence of a particular substance.

By using chloride as an additive in the solvent spray, the LOD was improved 1 order of magnitude, allowing the detection of a 10-pg RDX sample deposited on various plastic surfaces, floppy disk, computer hard drives, metal surfaces, cotton swabs, nitrile gloves, glass, and paper, all under the same experimental conditions. Only the two isotopic (RDX + Cl)$^-$ signals were observed in the spectrum at this concentration, but all surfaces produced these signals at this level. The floppy disk surface gave the strongest signals, possibly due to its electrical insulating properties.[35]

Nature of the RDX Adduct Ions at m/z 297 and 519. The RDX adduct ions at m/z 297 and at m/z 519 were shown by tandem mass spectrometry and isotopic labeling to be RDX molecules adducted to a hemiacetal anion of m/z 75. Analogous adducts have been observed in experiments involving other ionization methods, but there are conflicting claims in the literature on the elemental composition, structure, and provenance of this species. We report that, at least in the case of DESI, it is the hemiacetal which is involved and that it is produced by reaction between methanol and acetaldehyde, an impurity in methanol. The data and discussion that support this conclusion appear as Supporting Information.

HMX Sensitivity Enhancement Using Chloride Adduct Formation. The DESI technique was used for the detection of the secondary explosive HMX on the same surfaces used with the other explosives. Results obtained for HMX are in good agreement with those for RDX when comparing surfaces and amounts deposited. In the absence of added chloride in the spray solvent, relatively poor spectra were obtained. When 100 pg of HMX was
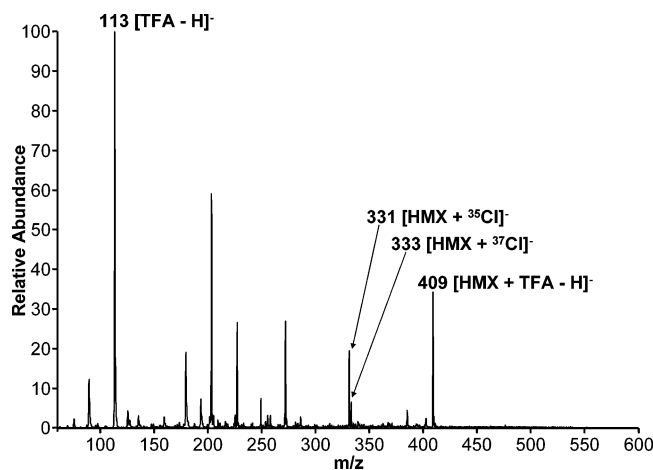
Figure 4. Negative ion DESI mass spectrum of 10 pg of HMX total amount deposited on paper in a total area of 1 cm^2 using methanol/water/TFA (1:1:0.05%) as the spray solvent. The adduct of HMX with TFA is observed at m/z 409.
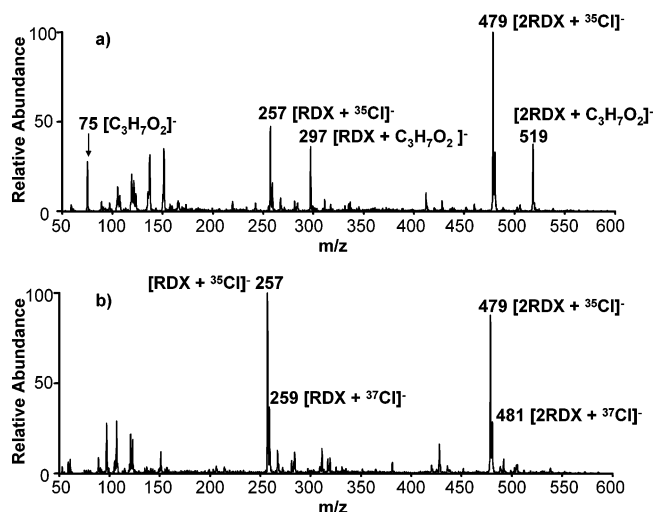

Figure 5. Negative ion DESI mass spectrum of 1 ng of RDX total amount deposited on paper in a total area of 1 cm^2 comparing (a) methanol/water and (b) water as spray solvents.

deposited on 1 cm^2 of paper, plastic, floppy disk, computer hard drive, or a nitrile glove surface, the chloride adduct was observed with the floppy disk surface producing the most intense peaks, as was also the case for RDX. Detection limits (S/N = 3) were 100 pg for plastic, floppy disk, computer hard drive, and nitrile from gloves, 10 pg for metal and cotton swabs, and 5 pg for paper. The mass spectrum for 100 pg of HMX (total amount deposited on an area of 1 cm^2 on a floppy disk) showed peaks corresponding to the adducts of HMX with chloride at m/z 331 and 333 in abundances of 29 and 10% relative to the m/z 75 base peak. The other major peak at m/z 371 (9% relative abundance) was examined by tandem MS and found to undergo loss of 76 mass units. This implicates the hemiacetal again in adduct formation.

RDX and HMX Sensitivity Enhancement by TFA Adduct Formation. TFA was also used as an additive in the spray solvent (methanol/water/TFA, 1:1:0.05%). TFA forms stable adducts with HMX and RDX at m/z 409 and 335, respectively, when these explosives are deposited on surfaces in trace amounts and ionized by reactive DESI. Figure 4 shows data for 10 pg of HMX deposited on paper and covering an area of 1 cm^2. The RDX data are analogous. Ions at m/z 331 and 333 in the HMX DESI spectrum are assigned as (HMX + ^{35}Cl)$^-$ and (HMX + ^{37}Cl)$^-$, respectively. The TFA anion (TFA − H)$^-$ was observed as the base peak in the negative ion DESI spectrum of HMX on paper. The limit of detection (S/N = 3) obtained for HMX by using TFA as an additive was 10 pg on paper. RDX forms a stable adduct at m/z 335 with the TFA anion under the same conditions as used for HMX. The adduct ion at m/z 335 fragments under CID conditions, giving rise to the TFA anion at m/z 113 by loss of an RDX molecule. The absolute detection limit (S/N = 3) obtained on paper using TFA as doping agent was 10 pg.

Other Aspects of DESI Explosives Analysis. *RDX Quantification on Paper.* Quantification of RDX on paper was performed by making a five-point calibration curve covering the range from 0.5 to 10 ng, as before, by depositing a particular amount of the sample on an area of 1 cm^2. The absolute abundance for the adduct ion at m/z 257 (RDX + ^{35}Cl)$^-$ was used to prepare the multipoint calibration curve because of its stability.[41] Triplicate measurements

showed a RSD of less than 3% (calibration curve: $y = 191.07x + 38.123$, $R^2 = 0.9998$). Using this calibration curve, an "unknown" RDX sample on paper was analyzed for RDX content. The average absolute abundance for triplicate measurements of the m/z 257 ion was used, which yielded a value of 3.58 ng as obtained from the calibration curve. The actual total amount of RDX deposited on paper was 3.5 ng, providing a rough idea of the accuracy of this single measurement.

RDX Ionization Using Water as Spray Solvent Instead of Methanol/Water. Potential safety concerns with the use of toxic compounds as spray solvents in DESI led to experiments being performed with pure water (Figure 5). First, a mixture of methanol/water (1:1) without additives was used as spray solvent and it showed characteristic adduct ions for RDX at m/z 519 (2RDX + C$_3$H$_7$O$_2$)$^-$, 479 (2RDX + ^{35}Cl)$^-$, 481 (2RDX + ^{37}Cl)$^-$, 297 (RDX + C$_3$H$_7$O$_2$)$^-$, 257 (RDX + ^{35}Cl)$^-$, and 259 (RDX + ^{37}Cl)$^-$ (Figure 5a). For these large sample sizes (1 ng of RDX deposited onto 1 cm^2 of paper), the base peak in the mass spectrum corresponds to the ion at m/z 479 rather than the monomeric adduct observed for 10-pg samples. The source of chloride is the water used in the solvent spray, the paper surface, or both.

In a second experiment, pure water without additives or methanol was used as the spray solvent (Figure 5b). Only the two major ions at m/z 479 and 257 and their isotopes were observed for the 1-ng RDX sample. These peaks correspond to the chloride adducts with RDX. This finding is easily interpreted as the result of the absence of the hemiacetal in the water used as spray solvent. As observed in Figure 5, using only water as the solvent spray for DESI, it is possible to obtain the same ionization efficiency as obtained using methanol/water (1:1). The main difference between both methods is the lack of adducts ions at m/z 297 and 519 corresponding to RDX adducts with the hemiacetal anion at m/z 75.

TNT Ion/Molecule Reactions. The ultimate goal in explosives detection is to develop sensitive and selective methods that allow the detection of explosives, even from complex matrixes. Forma-

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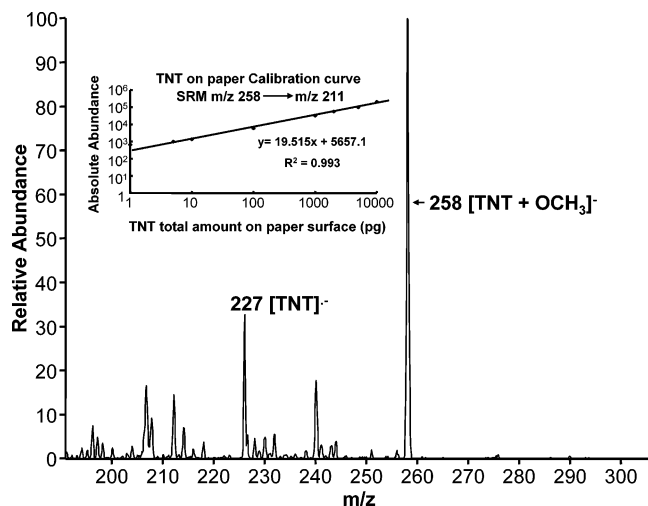
Figure 6. Negative ion DESI mass spectrum showing the formation of the Meisenheimer complex between TNT and the methoxide anion at m/z 258 when examining 10 pg of TNT deposited on paper in a total area of 1 cm². A 10 ppm solution of sodium methoxide in methanol was used as spray solvent. Inset is a calibration curve for TNT from 1 pg to 10 ng using single reaction monitoring of ion m/z 258 fragmenting to m/z 211 and showing a linear dynamic range of more than 3 orders of magnitude.

tion of the Meisenheimer complex of TNT is a highly selective reaction for TNT detection.[15] Figure 6 shows the negative ion DESI spectrum, which includes both the radical anion and the Meisenheimer complex with the methoxide anion $(OCH_3)^-$ when a trace sample (10 pg of TNT deposited on 1 cm² of paper) is examined. A 10 ppm solution of sodium methoxide in methanol was used as spray solvent. The identity of the adduct was confirmed by MS/MS, which showed the loss of 32 mass units corresponding to methanol loss producing the deprotonated TNT anion at m/z 226. Linearity was also investigated showing a linear range of more than 3 orders of magnitude (correlation coefficient of 0.993, inset to Figure 6).

DAPCI and Reaction Mechanisms. *Desorption Atmospheric Pressure Chemical Ionization of RDX and TNT.* RDX and TNT were analyzed using two different gaseous solvent vapors (toluene and methanol) both to examine the analytical performance of this variant method and also to investigate the DESI ion formation mechanism. Ion formation in DESI has been suggested to follow three different mechanisms depending on the conditions used and the particular analyte.[35] The first involves charge transfer between gaseous ions formed from the electrospray source and the analyte compound on the surface. The desorption of the analyte ions from the surface is thought to occur by a type of chemical sputtering.[42] The second mechanism (droplet pickup) involves impact of electrosprayed droplets on the surface, dissolution of the analyte at the surface onto or into the droplets, and then release of the droplets from the surface. Subsequent evaporation of the solvent and Coulomb fission generates ions by processes that parallel those that occur in conventional ESI. This accounts for the similarity of the DESI spectra with those of ESI in cases of proteins, where the pickup mechanism can be inferred to operate.

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The third mechanism of ion formation involves volatilization/desorption of neutral species from the surface followed by gas-phase ionization through proton/electron transfer or other ion/molecule reactions at atmospheric pressure. Transport of the analyte ions to the mass spectrometer may be facilitated by static charge accumulation on the insulating surface, momentum transfer in the course of the gaseous ion/charged microdroplet impact on the molecular species on the surface, and suction of the vacuum at the inlet of the transfer capillary.

To seek information on the DESI mechanism in the case of explosives, an experiment was performed in which explosives on surfaces were ionized by employing only gaseous reagents. DAPCI, which precludes the droplet pickup mechanism, has been briefly reported in a communication on explosives monitoring.[36] In this experiment, the electrospray emitter from the DESI source was replaced by a tapered stainless steel needle. Vapors of different solvents were mixed into the nitrogen gas flow, and a high voltage ranging from 3 to 6 kV was applied to the stainless steel needle. Ionization takes place at the stainless steel tip by corona discharge, generating reactant ions that then ionize the explosives molecules deposited on the surface. This ionization method shows results similar to DESI. The very low vapor pressures of the two explosives (RDX, 4.1×10^{-9}; TNT, 8.02×10^{-6} Torr) under ambient conditions probably preclude the gas-phase ionization mechanism. These results point to a DESI mechanism in which reagent ions formed by electrospray ionize the analyte molecules by either electron or proton transfer in a thermochemically controlled chemical sputtering step.[42] Vapor-phase reagent ions collide with the surface and electron, anion, or cation transfer from the reagent ions to the absorbed explosive occurs. The analyte is both ionized by the collision and also provided with a small amount of translational energy to help desorb it from the surface.

For either methanol or toluene vapor, DAPCI analysis of TNT (total amount 100 pg deposited on paper in a 1-cm² area) showed the radical anion at m/z 227 (TNT$^{\bullet-}$). Other species observed were m/z 92 and 77, corresponding to $C_7H_8^{\bullet-}$, and $C_6H_5^-$, respectively. Ionization was also achieved in the positive ion mode when toluene vapor was used as the reagent ion to examine RDX (100 pg total on paper in 1 cm²). The base peak in the positive ion DESI spectrum of RDX using toluene vapor was protonated RDX. Tandem MS was used to verify the identity of the ion at m/z 223, via the observed loss of a nitro group (NO$_2$). The ion at m/z 177 fragments in a succession of steps to give product ions at m/z 149, 121, and 93, each corresponding to losses of 28 probably CO, N$_2$, or CH$_2$N.

Using methanol vapor as the DAPCI reagent gas, RDX (100 pg deposited on paper, 1-cm² area) DESI-like spectra were recorded in the positive ion mode, the principal ion being protonated RDX. This is the expected result, given the higher proton affinity of RDX compared to methanol. This approach made it possible to record multiple stage data (up to MS⁴) for the ion m/z 223 (RDX + H)$^+$, the observed transitions being m/z 223 → 177 → 149 → 121 → 93. The first step corresponds to loss of a nitro group; the other three transitions probably correspond to CH$_2$N, CO, or N$_2$ losses, respectively. This result shows the high stability and sensitivity of the DAPCI method for positive RDX detection.
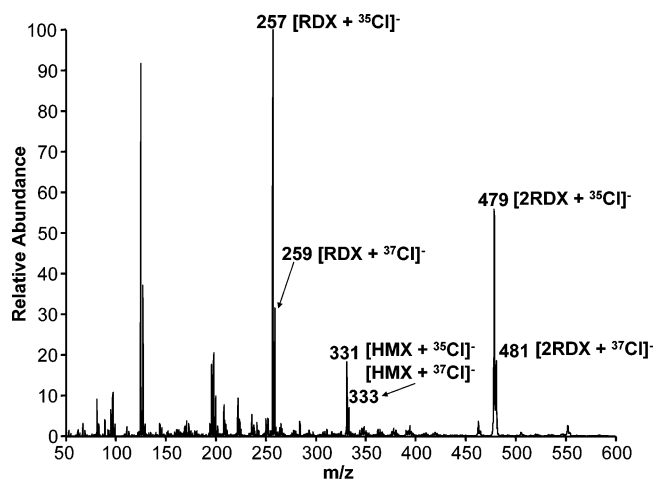
Figure 7. Negative ion DESI mass spectrum of 1 ng of C4 deposited on 1 cm^2 of metal using methanol/water/HCl (1:1:0.05%) as the spray solvent.

Figure 8. Negative ion DESI mass spectrum of 1 ng of Semtex-H deposited on Teflon in a total area of 1 cm^2 using methanol/water/HCl (1:1:0.05%) as the spray solvent.

Mixtures Containing Explosives. *Plastic Explosives.* Plastic explosive compositions (Composition C-4, Semtex-H, Detasheet) were analyzed by DESI on several surfaces without any sample preparation or manipulation. The spray solvent used for the analysis of all plastic explosives samples was a mixture of methanol/water (1:1) doped to a concentration 0.05% with HCl.

Composition C-4 is ~91% RDX (the composition varies with the manufacturer) plus ~5% bis(2-ethylhexyl) sebacate as plasticizer, 2% polyisobutylene as binder, and 1.6% motor oil; all of these are used to make the explosives easier to handle and reduce sensitivity to detonation by friction or impact.[2,43,44] The Composition C-4 negative ion DESI spectrum of a 1-ng sample deposited on metal over an area of 1 cm^2 is shown in Figure 7. This figure shows adducts formed from RDX and chloride at m/z 257 (RDX + ^{35}Cl)$^-$, 259 (RDX + ^{37}Cl)$^-$, 479 (2RDX + ^{35}Cl)$^-$, m/z 481 (2RDX + ^{37}Cl)$^-$. It is also possible to observe signals due to the minor component HMX found in Composition C-4 as a byproduct from the manufacture of RDX[43,44] as (HMX + ^{35}Cl)$^-$ and (HMX + ^{37}Cl)$^-$ at m/z 331 and 333, respectively.

Semtex-H is a plastic explosive based on RDX and PETN in approximately equal proportions (which vary with the manufacturer) plus antioxidant, plasticizer, dye, oil, and binder.[2,45] Figure 8 shows the negative ion DESI spectrum for 1 ng of Semtex-H deposited on Teflon in an area of 1 cm^2. The main ions seen in the spectrum correspond to the adducts (RDX + ^{35}Cl), (RDX + ^{37}Cl)$^-$, (PETN + ^{35}Cl), (PETN + ^{37}Cl), (2RDX + ^{35}Cl)$^-$, and (2RDX + ^{37}Cl)$^-$ at m/z 257, 259, 351, 353, 479, and 481, respectively. As in Composition C-4, both Semtex-H constituents effectively abstract chloride from the spray solution, forming stable adducts, and in this way increase the selectivity and sensitivity of their detection. It is worth noting that, for reasons not known, there are no m/z 75 or 297 (RDX + 75)$^-$ ions in the negative ion DESI spectra of Composition C4 (Figure 7) or of Semtex-H (Figure 8), even though these materials contain large amounts of RDX.
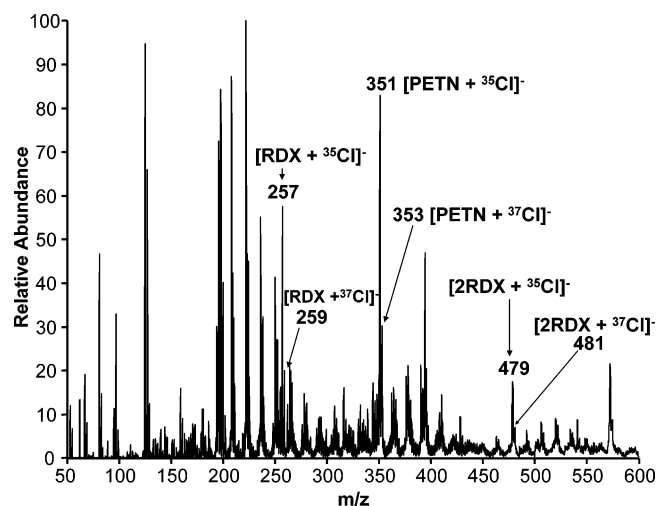
Detasheet, an explosive composed of PETN, a plasticizer, and an elastomeric binder,[2,43] was studied by DESI using the negative ion mode. The base peak in the mass spectrum of 1 ng of Detasheet deposited on metal in an area of 1 cm^2 occurs at m/z 351 and corresponds to the adduct of PETN and chloride (PETN + ^{35}Cl)$^-$ (data not shown). The ^{37}Cl isotopic peak was observed at m/z 353 in the expected 1:3 abundance ratio. The high abundance of the ion m/z 351 and its isotope at m/z 353, coupled with tandem MS data, increases the selectivity and helps in the rapid screening for the presence of trace amounts of this specific explosive (PETN), a Detasheet constituent, on the surface being analyzed.

Mixtures Containing Composition C-4, Detasheet, and Semtex-H. The ability to detect different explosives, accurately, selectively, sensitively, and rapidly is the final goal for any method to be used as a standard screening methodology. Selectivity is increased by tandem MS[46] using collision-induced dissociation, by ion/molecule reactions,[15,47–49] or through formation of adducts using specific deliberately added additives[22,23,25,40] that bind to the analyte. A sample containing three plastic explosives compositions (Composition C-4, Detasheet, Semtex-H) was deposited on a Teflon surface in a total amount of 500 pg of each. The main ions seen in the spectrum correspond to adducts of RDX, HMX, and PETN with chloride. Their identities were confirmed by MS/MS as (RDX + ^{35}Cl)$^-$, (RDX + ^{37}Cl)$^-$, (HMX + ^{35}Cl)$^-$, (HMX + ^{37}Cl)$^-$, (PETN + ^{35}Cl)$^-$, (PETN + ^{37}Cl)$^-$, (2RDX + ^{35}Cl)$^-$, and (2RDX + ^{37}Cl)$^-$, respectively.

Plastic Explosives Compositions in Complex Matrixes. In scenarios involving postblast analysis or airport screening, the sample to be analyzed may include hundreds of components, and this represents an additional challenge for selectively identifying

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explosives. The method employed should identify the unique spectral signatures of explosives while eliminating signals due to other components of these complex mixtures. Several matrixes (diesel, vinegar, Windex, WD-40, Clorox) were used as interferences in order to evaluate the performance of the DESI method to detect explosives in complex matrixes and on various surfaces such as paper or brick.

The negative ion DESI spectrum of 1 ng of Composition C-4 (total amount dissolved in diesel oil) and deposited on a brick surface over an area of 1 cm^2 includes adducts ions at m/z 257 and 259. Identities for these two ions were confirmed by tandem MS done on the brick and assigned as (RDX + ^{35}Cl)$^-$ and (RDX + ^{37}Cl)$^-$. They show the characteristic isotope ratio (3:1) of chlorine-containing compounds. The highly porous surface allows the sample to penetrate deeply, making analysis even more difficult. The same sample (1 ng of Composition C-4) and matrix (diesel oil) were analyzed on paper and showed similar adduct ions. Tandem MS again confirmed the composition of the adduct ions at m/z 257 and 259, corresponding to the previously seen chloride adducts with RDX.

For vinegar, WD-40, and Clorox matrixes, characteristic RDX adducts for 1 ng of Composition C-4 were observed for both paper and brick surfaces (1-cm^2 area). In the case of Windex, the minor component HMX found in Composition C-4 was also observed as an adduct with chloride at m/z 331 (HMX + ^{35}Cl)$^-$ and 333 (HMX + ^{37}Cl)$^-$ besides the (RDX + ^{35}Cl)$^-$ and (RDX + ^{37}Cl)$^-$ adducts ions (data not shown). For the 1-ng Composition C-4 sample dissolved in the Clorox matrix and deposited in an area of 1 cm^2, a better signal-to-noise ratio (4:1) was observed for adducts (RDX + ^{35}Cl)$^-$ and (RDX + ^{37}Cl)$^-$ at m/z 257 and 259, respectively, when compared to all previous matrixes and surfaces (S/N = 3). This can be attributed to the high chloride content in the mixture.

Fingerprints of Composition C-4 on Several Surfaces. The ability to detect fingerprints in situ from surfaces has been pursued with somewhat limited success using various spectroscopic methods[50–52] including optical methods based on microscope images to differentiate the sample particles from the background.[53] The use of DESI makes it possible to identify the major constituent RDX and its byproduct HMX.[43,44] Both constituents were found in fingerprints of Composition C-4 without any sample preparation or extraction[52] in situ from each of the surfaces tested, adding to the high sensitivity and selectivity of MS and the additional information available from adduct formation, ion/molecule reactions, and tandem MS.

Figure 9a shows the negative ion DESI spectrum for a Composition C-4 fingerprint on glass using methanol/water/HCl (1:1:0.05%) as spray solvent. Ions observed correspond to
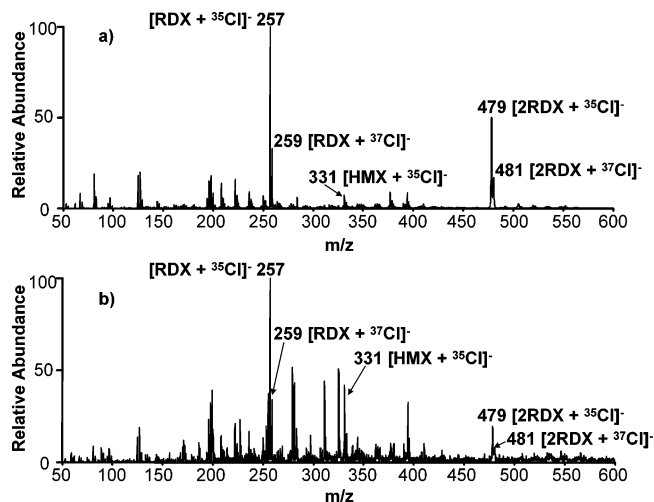
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Figure 9. (a) Negative ion DESI mass spectrum of a C4 fingerprint after impression onto a glass slide showing an intensity of 1.80 × 10^4 (arbitary units) for the adduct (RDX + ^{35}Cl)$^-$ ion at m/z 257. Methanol/water/HCl (1:1:0.05%) was used as the spray solvent. (b) Negative ion DESI mass spectrum of a C4 fingerprint after five transfers showing a total intensity of 1.04 × 10^3 for the adduct (RDX + ^{35}Cl)$^-$ ion at m/z 257.

(RDX + ^{35}Cl)$^-$, (RDX + ^{37}Cl)$^-$, (HMX + ^{35}Cl)$^-$, (HMX + ^{37}Cl)$^-$, (2RDX + ^{35}Cl)$^-$, and (2RDX + ^{37}Cl)$^-$, respectively, as confirmed by tandem mass spectrometry. The HMX present as a secondary product was observed in the negative DESI spectrum of Composition C-4 fingerprints. Figure 9b shows the negative ion DESI spectrum of a fingerprint after five transfers (see Experimental Section) onto a glass slide. The absolute abundance of the ion at m/z 257 (RDX + ^{35}Cl)$^-$ for the five transfers of the Composition C-4 fingerprint is more than 1 order of magnitude lower (1.04 × 10^3) than the absolute abundance of the original fingerprint (1.80 × 10^4). The spectrum shows ions similar to those in the first Composition C-4 fingerprint, and it shows a good signal-to-noise ratio (3:1) for the ion m/z 257, allowing several transfers to be performed.

CONCLUSIONS

Clearly, DESI can be used to detect trace amounts of explosives and its plastics compositions in either the positive or negative ion modes, in situ from a wide variety of surfaces (plastic, floppy disk, computer hard drive, metal, cotton swabs, nitrile gloves, glass, paper) by using appropriate spray solvents without any sample collection, handling, or preparation. The explosives can be detected in a wide variety of complex matrixes. The method is shown to be fast (<5 s), highly selective and sensitive, and gives absolute detection limits in the subnanogram to subpicogram range.

Addition of reagents to the spray solution (reactive desorption) represents an easy way to improve the selectivity for explosives detection by using additives that selectively bind to form characteristic adduct ions. In some cases, this approach improved the limits of detection 1 order of magnitude as compared to experiments where a simple solvent was sprayed. Using water as spray solvent, ionization efficiencies similar to those for mixtures of methanol/water were obtained. Fingerprints of explosives were also sampled from surfaces without any preparation, collection, or transfer step.

Initial observations on the mechanism of ionization of explosives by DESI suggest that in most cases ionization follows a chemical sputtering mechanism in which gas-phase reagent ions are formed in the electrospray. These reagent ions ionize the analyte molecules by attachment or by electron or proton transfer in a thermochemically controlled ionization step.

It is already known that high-throughput analysis (sampling rates of up to 10/s)[54] is possible using DESI. This raises the possibility that coupling DESI to a portable mass spectrometer may make a considerable contribution to transportation security. Recent advances in miniature mass spectrometers[55] increase the likelihood that a successful and sensitive device, similar in size to an IMS spectrometer but with much greater specificity, will be developed.

SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.