Identification of explosives and explosive formulations using laser electrospray mass spectrometry

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Mass analysis is demonstrated for the detection of sub-microgram quantities of explosive samples on a metallic surface at atmospheric pressure using laser electrospray mass spectrometry (LEMS). A non-resonant femtosecond duration laser pulse vaporizes native samples for subsequent electrospray ionization and transfer into a time-of-flight mass spectrometer. LEMS was used to detect 2,3-dimethyl-2,3-dinitrobutane (DMNB), 1,3,5-trinitrohydroxy-1,3,5-triazine (RDX), 3,4,8,9,12,13-hexaoxa-1,6-diazabicyclo[4.4.4] tetradecane (HMTD), and 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane (TATP) deposited on a steel surface. LEMS was also used to directly analyze composite propellant materials containing an explosive to determine the molecular composition of the explosive pellets at atmospheric pressure. Copyright © 2010 John Wiley & Sons, Ltd.
can be analyzed. These methods are therefore not suitable for analyzing the vast majority of native surfaces.

We have recently introduced a universal, laser-based mass spectroscopic technique known as laser electrospray mass spectrometry (LEMS) that overcomes several limitations of the direct analysis of native systems.\textsuperscript{32,33} Nanosecond laser pulses, utilized in other techniques such as LAESI and ELDI, employ a first-order resonant absorption to enable vaporization. However, since most molecules do not undergo resonant absorption using common nanosecond laser wavelengths, a matrix is added to the analyte to enable absorption of the laser pulse energy. In the LEMS method, a femtosecond (fs) non-resonant laser pulse is used, eliminating the need for a first-order resonant absorption and, thus, the need for a matrix.

Nanosecond laser pulses cause more thermal damage after interaction with a solid sample\textsuperscript{34} and more fragmentation in the gas phase\textsuperscript{35} than fs laser pulses under vacuum conditions. For example, when an 800 nm 130 fs laser pulse at 10\textsuperscript{13} W/cm\textsuperscript{2} impinges upon cryogenic multilayers of organic molecules on metallic substrates, vaporization of neutrals without fragmentation is observed with a translational energy of the order of 1 eV in the vaporized molecules.\textsuperscript{36} Additional investigations of cryogenic multilayer vaporization using fs duration lasers demonstrated that the quantity of molecules vaporized without fragmentation was inversely proportional to the pulse duration of the laser for a film thickness exceeding \(\sim 10\) monolayers.\textsuperscript{37} This is consistent with the picosecond laser pulse depositing energy into the substrate to enable vaporization. Thus, as the sample thickness was increased, a decrease in the number of vaporized molecules was observed because of the large increase in the degrees of freedom available in the overlay. On the other hand, a femtosecond duration laser couples directly into the molecular system resulting in an increase in the number of vaporized molecules with increasing sample thickness. This suggests that femtosecond lasers will be able to couple into any molecular system regardless of the background pressure.

The combination of non-resonant femtosecond vaporization of molecules with electrospray ionization to transfer the vaporized sample into a mass spectrometer results in a new method for macromolecule analysis. Non-resonant femtosecond vaporization has been demonstrated for biomolecules adsorbed on a glass surface with molecular weight up to 1355 Da (vitamin B12) and for pharmaceuticals and narcotics adsorbed on metal, glass, wood, and cloth surfaces.\textsuperscript{32,33} The vaporization occurs with limited fragmentation and, more importantly, without the aid of a matrix. Thus, LEMS is capable of coupling into all films without the need for resonant first order absorption, and can analyze such samples at ambient, atmospheric pressure.\textsuperscript{32,33}

Here, we present the use of LEMS to detect a taggant and explosives adsorbed on metal surfaces without the aid of a matrix or a resonant transition. We investigate the analysis of 2,3-dimethyl-2,3-dinitrobutane (DMNB), RDX, HMTD, and TATP deposited on a stainless steel substrate. We also demonstrate the analysis of an explosive propellant mixture directly from a pellet formulation.

**Figure 1.** The structures and molecular weights of the taggant and explosive molecules analyzed: (a) 2,3-dimethyl 2,3-dinitrobutane (DMNB), (b) 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX), (c) 3,4,8,9,12,13-hexaoxa-1,6-diazabicyclo[4.4.4]tetradecane (HMTD), and (d) 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane (TATP).

**EXPERIMENTAL**

**Sample preparation**

The structures and the molecular weights of the taggant and explosives analyzed are shown in Fig. 1. Samples of DMNB, RDX, HMTD and TATP (AccuStandard, New Haven, CT, USA) were obtained in a dilute acetonitrile/methanol (1:1) solution and were prepared by drying a 50 \(\mu\)L aliquot of 10\textsuperscript{–4} M (50 \(\mu\)L of 10\textsuperscript{–3} M for RDX) on a stainless steel slide. This results in the deposition of approximately 5 \(\mu\)g, 24 nmol (50 \(\mu\)g, 224 nmol for RDX) of material in an even film covering approximately 1 cm\textsuperscript{2}. To analyze a complex mixture, a 0.16 cm\textsuperscript{2} x 0.4 cm piece of propellant containing RDX, plasticizers and binders was placed on a stainless steel slide. The sample slides were placed on a metal plate in the ESI source chamber. The metal plate was supported by a three-dimensional translation stage which permits the analysis of fresh sample with each laser shot.

**Mass spectrometry**

The mass spectrometer system was constructed as described previously.\textsuperscript{32} Briefly, the system comprises an ESI source for ionizing and transferring vaporized sample into a vacuum chamber where pulsed deflection orthogonal time-of-flight (o-TOF) separation of the ions is performed. The ESI source from Analytica of Branford (Branford, CT, USA) employs a grounded needle, a dielectric capillary (both ends coated with metal) biased to \(-5300\) V, a skimmer and a hexapole operated in the trapping mode where the positive ions are collected at 10 Hz. The electrosprayed ions enter the dielectric capillary before passing through the skimmer. The ions then enter a linear hexapole where they are trapped for 250 ms before being pulsed out of the source and transferred to the extraction region by a second hexapole (Ardara Technologies, North Huntingdon, PA, USA). The ions are transferred from the second hexapole to the extraction region of the linear o-
TOF analyzer (Jordan TOF Products Inc., Grass Valley, CA, USA) using a set of ion optics (Ardara Technologies). The ions are then pulsed orthogonally with respect to the electrospray ion optics into the TOF analyzer using two high-voltage pulser s. The extraction region and field-free flight tube were maintained at a pressure of 10⁻⁶ Torr. The positive ions were detected using microchannel plates in a Chevron configuration. The resulting positive ion mass spectrum, with a resolution of m/Δm ~180, was averaged for 50 laser shots using a digital oscilloscope.

An electrospray solvent mass spectrum was acquired before each experiment and subtracted from the LEMS measurement to produce the spectra shown. The vaporized molecules compete for the charge in the electrosprayed solvent, causing a change in the observed solvent cluster distribution. This leads to the formation of negative and/or positive solvent features seen in the subtracted mass spectra. Only peaks that are not solvent-related are labeled in the figures.

The ESI o-TOF system was mass-calibrated in positive ion mode using an electrospray tuning solution (Agilent Technologies Inc., Santa Clara, CA, USA) containing molecules that will produce ions ranging in m/z from 100 to 3000. A quadratic calibration was performed using software (Labview 8.5) written in-house to ensure the accuracy of the m/z scale.

**Vaporization and ionization apparatus**

A Ti:Sapphire oscillator (KM Labs Inc., Boulder, CO, USA) seeded a regenerative amplifier (Coherent Inc., Santa Clara, CA, USA) to create 70 fs laser pulses centered at 800 nm with a pulse energy of 2.5 mJ. The laser pulse energy was reduced to 400 μJ/pulse using a neutral density filter. The 1 kHz repetition rate of the laser was reduced to 10 Hz to couple to the electrospray system. The non-resonant femtosecond laser pulse was directed at the sample to induce vaporization of the explosive material. The laser was focused to a spot size of 250 μm in diameter using a 17.5 cm focal length lens, with an incident angle of 45° with respect to the sample (Fig. 2). The intensity of the laser on the sample was approximately 10¹³ W/cm². The metal sample plate holder was biased to −2 kV to correct for the distortion in the electric field between the needle and capillary inlet caused by the sample plate. This bias optimizes the entrance current of the ions into the dielectric capillary. The vaporized sample was captured and ionized by electrospraying methanol/water (7:3) containing 0.5% sodium chloride and potassium chloride, perpendicular to the laser-vaporized plume trajectory. The electrospray solvent flow rate was 3 μL/min as set by a syringe pump. The electrosprayed solvent was dried by counter-current nitrogen gas at 180°C before entering the inlet capillary.

**Safety considerations**

Due to the nature of explosive samples, small volumes were deposited on the surface and otherwise stored in dilute solutions. Appropriate laser eye protection was worn by all personnel and the high voltage area was enclosed in plexiglass to prevent accidental contact with the biased electrodes.

**RESULTS AND DISCUSSION**

Previous investigations using DESI revealed that explosives are difficult to detect due to the low probability of forming their [M+H]⁺ ions. However, when sodium or potassium is added to the electrospray solvent, detection sensitivity increases due to the formation of stable sodiated and potassiated adducts with the explosives. The formation of similar adducts with the taggant molecule also enables their detection. The formation of stable adducts with explosives is demonstrated using LEMS for the analysis of DMNB, as shown in Fig. 3. The [M+Na]⁺ and [M+K]⁺ adducts of DMNB are observed at m/z 199 and 215, respectively. The features

![Figure 2. Schematic of the non-resonant laser vaporization and electrospray ionization apparatus. The analyte is vaporized from a sample plate holder mounted to a three-dimensional translation stage.](image)

![Figure 3. The mass spectrum resulting from analysis of a 50 μL aliquot of 10⁻³ M DMNB dried on a metal surface. Sodium and potassium adducts of DMNB are detected in the spectrum at m/z 199 and 215, respectively.](image)
projecting toward negative intensity below the baseline in the spectrum at \( m/z \ 81, 124 \) and \( 136 \) are due to the subtraction procedure employed to remove the intense solvent-related peaks in the mass spectrum so that the sample-related features may be observed.

The DMNB molecule has a relatively high vapor pressure (\( \sim 10^{-3} \) Torr at 298 K)\(^{39} \) and it is used as a taggant for explosives. This signature molecule is beneficial because many explosives have very low vapor pressures. For instance RDX and trinitrotoluene (TNT) have vapor pressures of \( \sim 10^{-6} \) and \( \sim 10^{-8} \) Torr, respectively, at 300 K.\(^{40} \) A taggant, such as DMNB, is required by US law to be added to all commercially produced plastic explosives made in the United States,\(^{41,42} \) because of a high response in the IMS measurement.\(^{43} \) The addition of a taggant reduces the amount of air required for sampling when SPE, puffers or vacuuming are used to collect signature molecules emitted by explosive materials. Such high vapor pressure signatures increase the probability of detection due to their higher abundance in the sampled air. The detection of DMNB demonstrates that LEMS is effective for sampling explosives containing high vapor pressure taggants with the appropriate electrospray solvent. Control experiments demonstrate that a relatively high vapor pressure allows direct entrainment of DMNB in the electrospray plume, and its detection in the mass spectrometer, even in the absence of laser vaporization.

Currently, most mass analysis instruments used to detect explosives cannot investigate a surface directly. Swabs are used in most solid probing methods to transfer materials from the surface to the analysis instrument.\(^{16,44} \) We next investigated whether LEMS allows the direct investigation of an explosive-contaminated solid surface without the need for wiping or an elution step. The LEMS spectrum from 50 \( \mu L \) of \( 10^{-3} \)M RDX deposited on a stainless steel substrate is shown in Fig. 4. The addition of sodium and potassium to the electrospray solvent was required for the detection of the adducts of RDX. (An acidified electrospray solvent resulted in no detectable ions from protonated RDX.) The [M + Na]\(^+ \) and [M + K]\(^+ \) ions of RDX are observed at \( m/z \ 245 \) and 261, respectively. Detection of these sodiated and potassiated adducts of RDX reveals that intense, fs duration lasers can be used to transfer explosives from the condensed phase into the gas phase without fragmentation. The fact that there is no matrix added and no first order absorption resonant at 800 nm suggests that the vaporization occurs through a non-resonant coupling mechanism. Previous investigations of biomolecules\(^{52} \) have revealed that the vaporization can also occur on transparent dielectrics, suggesting that the laser couples directly into the analyte in the LEMS process. The peak at \( m/z \ 379 \) (marked with an asterisk) is not observed in the solvent background spectrum and is attributed to a fragment of a dimer of RDX. The linear TOF mass spectrometer employed in these studies cannot perform the MS\(^{3} \) experiments needed to confirm the identity of this peak.

To confirm the ability of LEMS to detect explosives and to determine the sensitivity of LEMS from undiluted commercially available explosive standards, 5 \( \mu g \) HMTD (50 \( \mu L \)) and 25 \( \mu g \) of RDX (25 \( \mu L \)) were deposited onto separate steel surfaces, with each spot covering an area of 0.6 cm\(^2 \). Using the previously described method\(^{35} \) of optical imaging before and after laser vaporization we estimate that approximately 8 ng (~38 pmol) of HMTD and 24 ng (~110 pmol) of RDX were vaporized from the sample surface per laser shot. Approximately 50 laser shots are required to routinely discriminate each explosive using LEMS. In the case of RDX, 112 nmol was deposited, and 4% of the deposited sample (200–1000 ng) was consumed in the analysis. Thus, LEMS analysis of explosive materials has nanogram sensitivity, without dilution of the commercially available standard. The sensitivity reported here should not be taken as the absolute sensitivity of the LEMS technique. The limit of detection ultimately depends on laser parameters (wavelength, pulse duration, intensity, etc.), mass spectral sensitivity (linear TOF vs. reflectron TOF vs. orbitrap), amount of material deposited, explosive film morphology and chemical noise due to interferants.

The energetic ingredient in a formulation (containing plasticizers, stabilizers and/or binders) often has a lower vapor pressure than the energetic ingredient in its pure form. This makes gas-phase sampling and detection methods more challenging and suggests that direct probing of the solid phase is a desirable detection strategy. To explore the direct analysis of an explosive in a formulation we investigated an RDX-based propellant using LEMS. Figure 5 shows the mass spectrum measured for a propellant composed of RDX, ethyl centralite (a stabilizer) and nitrocellulose directly subjected to vaporization by the non-resonant laser pulse. The [M + Na]\(^+ \) and [M + K]\(^+ \) adducts of RDX are detected at \( m/z \ 245 \) and 261, respectively. An RDX fragment ion, \([C_3H_7N_2O_2]^+ \), is also observed, at \( m/z \ 128. \)\(^{45} \) The peaks at \( m/z \ 269, 291 \) and 307 correspond to protonated, sodiated and potassiated ethyl centralite, respectively. The difference in the signal intensity between the RDX adducts and the ethyl centralite adducts suggests that the explosive material does not have

**Figure 4.** The mass spectrum resulting from analysis of a 50 \( \mu L \) aliquot of \( 10^{-3} \) M RDX dried on a metal surface. The sodium and potassium adducts of RDX are detected in the spectrum at \( m/z \ 245 \) and 261, respectively. The peak at \( m/z \ 379 \) (marked \( \ast \)) is not observed in the solvent background and is attributed to a fragment of a dimer of RDX.
a high probability of forming positive ions during the electrospray ionization process. The nitrocellulose contained in the propellant was not observed when the methanol/water (1:1) solution containing 0.5% sodium chloride and potassium chloride was used as the electrospray solvent. Using the acidified solvent (methanol/water (1:1) with 1% acetic acid), no ions attributed to RDX were detected. The observation of ethyl centralite was independent of the solvent system used.

Detection of fragile peroxide explosives is becoming increasingly important due to the relative ease with which these can be synthesized with common chemicals. When mass spectral methods are used for such peroxides, extensive fragmentation typically occurs. The ability to detect the [M+H]$^+$, [M+Na]$^+$ or [M+K]$^+$ ions is important for reducing false positive and false negative alarm rates. Thus, we investigated the analysis of peroxide-based explosives including HMTD and TATP using LEMS. The mass spectrum obtained from a 50 $\mu$L aliquot of 10$^{-4}$ M HMTD deposited onto a steel substrate is shown in Fig. 6. The [M+Na]$^+$ and [M+K]$^+$ ions of HMTD are observed along with several fragment ions. The peaks at m/z 229 [M–2H+Na]$^+$ and m/z 245 [M–2H+K]$^+$ suggest the loss of two hydrogen atoms. Although there is more fragmentation observed in the mass spectrum of HMTD than in the spectrum of RDX, the detection of the sodiated and postassiated adducts of HMTD using LEMS suggests that a non-resonant laser pulse of fs duration is capable of transferring this rather fragile molecule into the gas phase for subsequent mass spectral analysis, without fragmentation.

The mass spectrum resulting from the analysis of TATP reveals considerable fragmentation as well as the presence of the sodiated and postassiated TATP dimer ions at m/z 467 and 483, respectively (Fig. 7). The [M+H]$^+$, [M+Na]$^+$ or [M+K]$^+$ ions were not observed under the conditions employed in this study which is consistent with the significant instability of this particular molecule. We do not have independent confirmation that the TATP sample dissociated upon deposition. While the fragments of TATP cannot be uniquely identified using our linear TOF instrument, a list of proposed formulae consistent with the m/z values of the observed fragment ions is included in Supplementary Table S1 (See Supporting Information).
The listed fragment ion masses are not observed in the background solvent spectrum and they are therefore attributed to TATP. Finally, we note that the rich fragmentation spectrum presented in Fig. 7 serves as a fingerprint for the TATP explosive.

CONCLUSIONS

The universal detection of explosive materials is difficult due to the wide variety of chemical structures and the often exceedingly low vapor pressures. We demonstrate here that the combination of femtosecond laser vaporization with electrospray ionization and time-of-flight mass spectrometry provides a new method to detect explosives and explosive formulations. This method circumvents the challenge of detecting a low vapor pressure molecule by inducing vaporization into the gas phase with non-resonant, ultrafast femtosecond laser excitation. We have shown that LEMS is capable of detecting sub-microgram quantities of RDX, HMTD and TATP, as well as the explosive signature molecule DMNB. We demonstrate a new release technology based on non-resonant laser vaporization of explosive molecules from metal surfaces using a 70 fs, 800 nm laser pulse. Once vaporized, the molecules were ionized using ESI and detected using TOF-MS. LEMS is capable of detecting at least ~8 ng of explosive from undiluted commercially available standard.

SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article.

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REFERENCES