

Detecting Trace Explosives and Formulations Using Laser Electrospray Mass Spectrometry

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Mass analysis using laser electrospray mass spectrometry (LEMS) is demonstrated for the detection of trace samples of explosives at atmospheric pressure directly from a substrate. A non-resonant femtosecond duration laser pulse vaporizes native samples at atmospheric pressure for subsequent electrospray ionization and transfer into a mass spectrometer. LEMS was used to detect < 1 μg of 2,3-dimethyl-2,3-dinitrobutane (DMNB), cyclotrimethylene-trinitramine (RDX), hexamethylene triperoxide diamine (HMTD), and triacetone triperoxide (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 intact pellets at atmospheric pressure.

The detection of trace amounts of unknown explosive materials is a major challenge for any single analytical technique due to the wide variety of chemical structures and the enormous range of vapor pressures (ranging from torr to picotorr at room temperature) for potential samples of interest. Explosives are typically detected either directly in the gas phase or on a surface via a transfer step using a wipe.¹ Due to the extremely low vapor pressure of most explosive molecules, most gas phase methods require a large volume of air to be sampled with puffers or air sampling pumps.^{2,3} Solid phase extraction (SPE) is typically employed to pre-concentrate the explosive from the gas phase onto a high surface area sorbent for subsequent analysis. The collected sample is then released by rapid heating or solvent elution and analyzed using a variety of methods including gas chromatography,⁴⁻⁶ Raman spectroscopy,⁷⁻¹⁰ or ion mobility spectrometry (IMS).¹¹⁻¹³ Because of the extreme sensitivity to many explosive molecules, IMS is the most commonly employed detection method under atmospheric pressure conditions. In a typical analysis, a swab is taken of the item to be interrogated (suitcase, briefcase, laptop, etc.) and analyzed.¹⁴ However, the high rate of false positives and false negatives for all existing detection technologies motivates the investigation of additional sampling and detection methods that are not prone to interferences. An ideal analysis method would be fast, sensitive, accurate and work for the widest variety of explosive materials.

The direct mass spectral analysis of explosive materials at atmospheric pressure with no sample preparation is of particular interest because this enables probing of the native state of molecules on the substrate. This has the potential to decrease the probability for a false negatives because no sample is lost during the collection and processing steps, via incomplete transfer to the swab or thermal degradation during thermal vaporization, for example. Several methods have been developed to directly analyze materials and surfaces at atmospheric pressure. Desorption

electrospray ionization (DESI) uses an electrospray directed at a sample surface to transfer analytes to the gas phase using a droplet pick-up mechanism.^{15, 16} DESI has been used to detect a variety of explosives including: hexamethylene triperoxide diamine (HMTD),¹⁷ triacetone triperoxide (TATP),¹⁷ octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX),¹⁸ 2,4,6-trinitrotoluene (TNT),¹⁸ pentaerythritol tetranitrate (PETN)¹⁸ and cyclotrimethylene-trinitramine (RDX).¹⁸ DESI has been demonstrated to be a sensitive method for detecting a variety of molecules at concentrations as low as 20 fmol for explosives.¹⁹ Several laser-based techniques have also been developed recently including electrospray-assisted laser desorption ionization (ELDI),^{20, 21} laser ablation electrospray ionization (LAESI),^{22, 23} and matrix-assisted laser desorption electrospray ionization (MALDESI).²⁴⁻²⁶ These techniques use lasers that are resonant with either the matrix or substrate, limiting the samples that can be analyzed. These methods require the presence of a specific matrix molecule, such as 2,3-dihydroxybenzoic acid, or water, and thus, are not amenable to 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 direct analysis of native systems.^{27, 28} In this method, an intense, femtosecond (fs) non-resonant laser pulse interacts with a given material and vaporizes intact molecules into the gas phase, regardless of the molecular composition. When an 800 nm 130 femtosecond laser at 10^{13} W/cm² impinged on cryogenic multilayers of organic molecules on metallic substrates, vaporization of intact neutrals with translational energy on the order of 1 eV was the only channel detected in the gas phase.²⁹ The combination of non-resonant neutral desorption with electrospray ionization to transfer the sample into a mass spectrometer resulted in a new method for macromolecule analysis with useful properties including the ability to transfer large molecules (>1000 amu) into

the gas phase intact without the need for matrix, the ability to couple into all films without the need for resonant first order absorption, and the ability to analyze such samples while working in ambient, atmospheric pressure. The LEMS method has been used to analyze matrix free biomolecules adsorbed on a glass surface with molecular weight up to 1355 amu (vitamin B12) and trace amounts of pharmaceuticals and narcotics adsorbed on metal, glass, wood and cloth surfaces.^{27,28}

Here we present the use of LEMS to detect trace amounts of taggants and explosives adsorbed on metal surfaces. 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 a propellant mixture directly from the pellet formulation.

EXPERIMENTAL METHODS

Sample Preparation. 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 μL aliquot of 10^{-4} M (50 μL of 10^{-3} M for RDX) on a stainless steel slide. This results in the deposition of approximately 5 μg , 24 nmol (50 μg , 224 nmol for RDX) of material in an even film covering approximately 1 cm^2 . To analyze a complex mixture, a 0.16 cm^2 x 0.4 cm piece of propellant containing RDX, plastizers and binders was placed on a stainless steel slide. The stainless steel 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 on each laser shot.

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 μ J/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 laser was focused to a spot size of 250 μ m in diameter using a 17.5 cm focal length lens, with an incident angle of 45° with respect to the sample. The intensity of the laser on the sample was approximately 10^{13} W/cm². The ablated sample was captured and ionized by electrospraying 70/30 methanol/water containing 0.5% sodium chloride and potassium chloride. The electrospray solvent flow rate was 3 μ l/min as set by a syringe pump. The source setup and parameters are described elsewhere.^{27, 28} The resulting positive ion mass spectrum was collected for 50 laser shots using a digital oscilloscope and averaged to obtain the signal to noise displayed.

The ESI o-TOF system was mass calibrated using a quadratic calibration performed in our software by electrospraying a calibration solution (Agilent Technologies Inc., Santa Clara, CA, USA) with molecules ranging from $m/z = 100$ to 3000 amu.

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

The LEMS analysis of DMNB is shown in Figure 1 and the parent molecular ions of $[M+Na]^+$ and $[M+K]^+$ are both observed at $m/z = 199$ and 215 , respectively. Remarkably, the intact ion is observed at the high intensity 10^{13} W/cm^2 employed for the vaporization. The sodium and potassium adducts are observed because of the addition of NaCl and KCl to the solvent to enable detection. Previous investigations using DESI revealed that protonated explosives are difficult to detect do to low proton affinity.¹⁷ However, when sodium or potassium is added to the electrospray solvent, detection sensitivity increases due to the formation of stable adducts with the explosives.^{17, 18, 30} Similar formation of adducts with taggant molecules allows their detection. The negative going features in the spectrum are due to the subtraction procedure employed to remove the solvent-related peaks in the electrospray mass spectrum to reveal the sample-related features.

The molecule DMNB has a relatively high vapor pressure ($\sim 10^{-3}$ torr) and is therefore a common signature molecule for military explosives. This signature molecule is required because many explosives, RDX and trinitrotoluene (TNT) in particular, have very low vapor pressures, $\sim 10^{-6}$ and $\sim 10^{-8}$ Torr, respectively at 300 K.³¹ DMNB is added to all commercially produced explosives because of the sensitive response in the IMS measurement.³² The addition of a taggant, such as DMNB, reduces the amount of air required for sampling when solid phase extraction, puffers or vacuuming are used to collect signature molecules emitted by explosive materials. Such high vapor pressure compounds increase detection probability 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

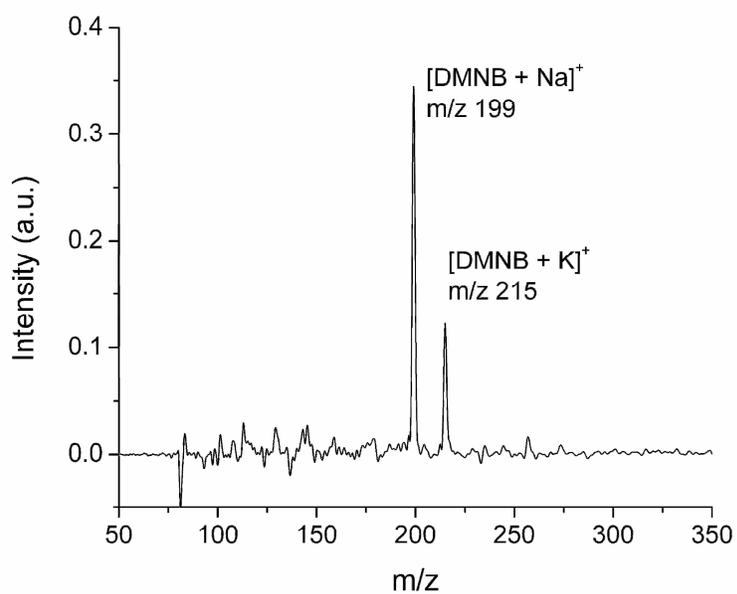


Figure 1. A 50 μL aliquot of 10^{-4}M DMNB was spotted and dried on a metal surface. Complexes of sodium and potassium with DMNB are both seen in the spectrum at $m/z = 199$ and 215, respectively.

entrainment of DMNB in the electrospray plume, and detection in the mass spectrometer, even in the absence of laser vaporization.

Most analysis instruments used to detect explosives can not currently investigate a surface directly. Wipes are used in most solid probing methods to transfer materials from the surface to the analysis instrument, such as an IMS.^{14, 33} We next investigate whether LEMS allows the direct investigation of a explosive contaminated solid surface without the need for wiping or elution step. The LEMS mass spectrum from 50 μL of 10^{-3} M RDX deposited on a stainless steel substrate is shown in Figure 2. The stable RDX adducts, $[\text{M}+\text{Na}]^+$ and $[\text{M}+\text{K}]^+$, are observed at $m/z = 245$ and 261 , respectively. This experiment reveals that intense, femtosecond duration lasers can be used to transfer explosives from the condensed phase into the gas phase intact through a non-resonant coupling mechanism. We note that previous investigations of biomolecules reveal that the vaporization occurs on transparent dielectrics as well, suggesting that the laser couples directly into the analyte in the LEMS process. The peak at $m/z = 379$ is consistent with a dimer of fragmented RDX. However, the linear TOF employed in these measurements can not perform the MS/MS technique needed to confirm the identity of the peak. The addition of sodium and potassium to the electrospray solvent was required for detection of intact molecular ions. An acidified electrospray solvent resulted in no detectable parent molecular ions.

To confirm the ability of LEMS to detect explosives and to determine the sensitivity of LEMS for explosive materials, 5 μg HMTD (50 μL) and 25 μg of RDX (25 μL) were deposited onto separate steel surfaces, with each spot covering an area of 0.6 cm^2 . Using the previously described method²⁸ of optical imaging before and after laser vaporization we estimate that

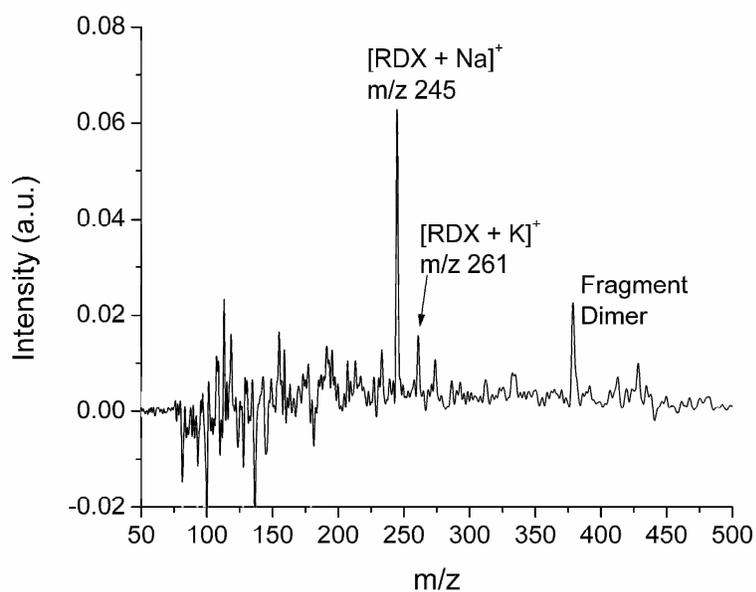


Figure 2. A 50 μL aliquot of 10^{-3}M RDX (Cyclotrimethylene-trinitramine) was spotted and dried on a metal surface. The complexes of sodium and potassium with RDX are both seen in the spectrum at $m/z = 245$ and 261 , respectively. A fragment dimer is speculated at $m/z = 379$.

approximately 8 ng (~ 38 pmol) of HMTD and 24 ng (~ 110 pmol) of RDX was 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, with 5 nmol consumed for the analysis. LEMS analysis of explosive materials has shown that the technique has nanogram sensitivity, without dilution of the commercially available standard. The limit of detection ultimately depends on laser parameters, mass spectral sensitivity, explosive film morphology and clutter due to interferants.

The main energetic ingredient in a formulation containing plasticizers, stabilizers or binders often has a lower vapor pressure than the neat material. The overall vapor pressure will be higher if the binder or plasticizer has a higher vapor pressure than the main energetic ingredient. The former case makes gas phase sampling and detection methods more challenging and time consuming. This suggests that when possible, a direct probing of the solid phase is desirable as a detection strategy. To explore the direct analysis of an explosive in a binder we investigate an RDX-based propellant using LEMS. Figure 3 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 parent ion of RDX is detected as the alkali atom adducts $[M+Na]^+$ and $[M+K]^+$ at $m/z = 245$ and 261 , respectively. An RDX fragment, $[C_3H_4N_4O_2^+]$, is also observed, at $m/z = 128$.³⁴ There are a series of ion peaks that are detected at $m/z = 269$, 292 , and 308 that correspond to the protonated, sodium and potassium adducts of 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 a high probability to form positive ions during the electrospray ionization process.

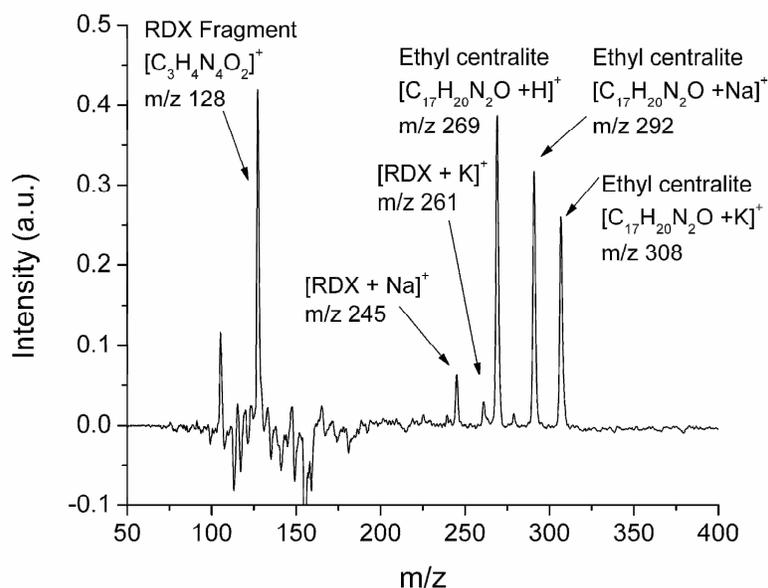


Figure 3. An RDX formulation contains 76% RDX, 4% nitrocellulose and 20% binders, stabilizers (ethyl centralite), and propellants. The complexes of sodium and potassium with RDX are both seen in the spectrum at $m/z = 245$ and 261 , respectively. The most intense peaks are the protonated ethyl centralite ($m/z = 269$), the sodium complex with ethyl centralite ($m/z = 292$) and potassium complex with ethyl centralite ($m/z = 308$). An RDX fragment is also seen at $m/z = 128$.

The nitrocellulose contained in the propellant was not observed when 50/50 methanol/water containing 0.5% sodium chloride and potassium chloride was used as the electrospray solvent. However, a solution employing a 50/50 methanol/water containing 1% acetic acid does provide nitrocellulose signal in the positive ion mode (data not shown). Using the acidified solvent, no RDX signal was 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.³⁵ The ability to detect intact parent adduct 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 our new method. The LEMS mass spectrum, from a 50 μ L aliquot of 10^{-4} M HMTD deposited onto a steel substrate, is shown in Figure 4. The parent adduct ions, $[\text{HMTD}+\text{Na}]^+$ and $[\text{HMTD}+\text{K}]^+$, are observed along with several fragment peaks. The peaks at $m/z = 229$ $[\text{HMTD}-2\text{H}+\text{Na}]^+$ and $m/z = 245$ $[\text{HMTD}-2\text{H}+\text{K}]^+$ suggest the loss of two hydrogen atoms during the vaporization or ionization process. The fragment peaks of HMTD at $m/z = 128$, 145 and 179 are consistent with literature values for the $[\text{M}+\text{Na}-\text{C}_3\text{H}_7\text{NO}_3]^+$, $[\text{M}+\text{H}-\text{HCHO}-\text{H}_2\text{O}_2]^+$ and $[\text{M}+\text{H}-\text{HCHO}]^+$ fragments.¹⁷ While there is more fragmentation detected in the HMTD peroxide in comparison with RDX, the detection of intact peroxide explosive using LEMS suggests that a non-resonant laser pulse of femtosecond duration is capable of transferring this rather fragile molecule into the gas phase for subsequent mass spectral analysis.

The mass spectrum resulting from the analysis of TATP, Figure 5 contained in the supporting information, reveals considerable fragmentation as well as the presence of the sodium and

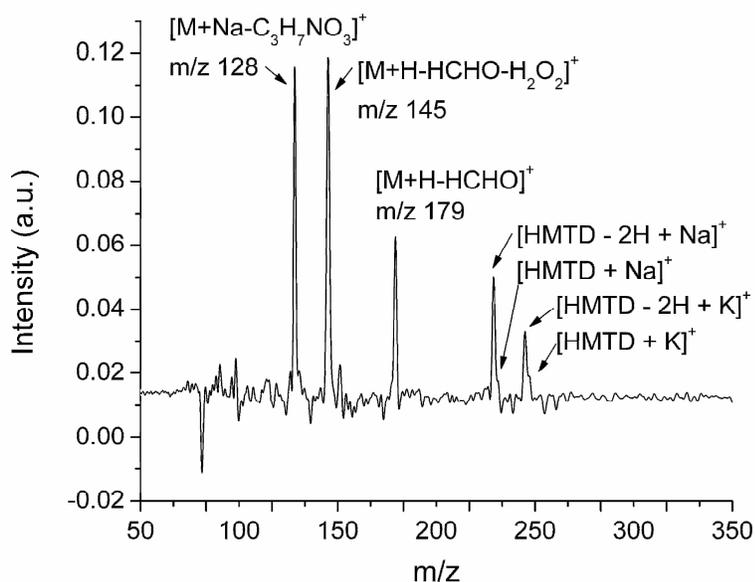


Figure 4. A 50 μ L aliquot of 10^{-4} M HMTD (Hexamethylene triperoxide diamine) was spotted and dried on a metal surface. The sodium and potassium adducts form complexes with HMTD, making detection possible. The peaks at $m/z = 229$ $[HMTD-2H+Na]^+$ and $m/z = 245$ $[HMTD-2H+K]^+$ suggest the loss of two hydrogen atoms. Fragment peaks of HMTD at $m/z = 128$, 145 and 179 are consistent with reported literature values.

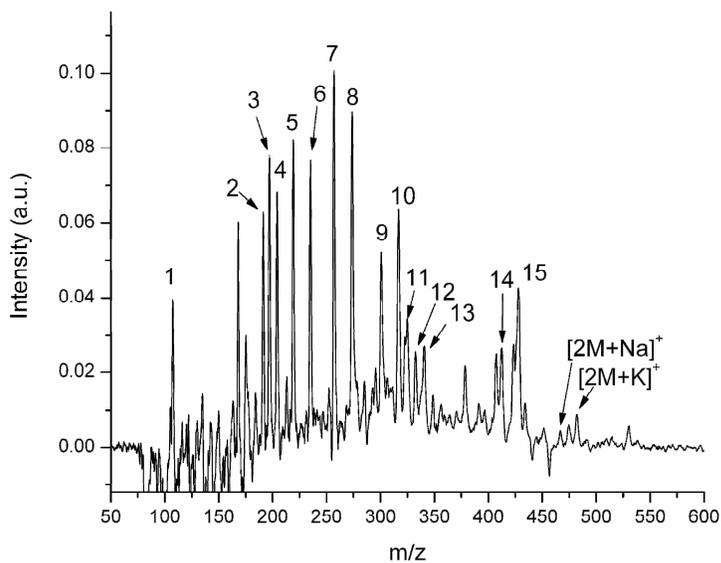


Figure 5. A 50 μL aliquot of 10^{-4}M TATP (triacetone triperoxide) was spotted and dried on a metal surface. Interaction of the laser with TATP causes a high degree of fragmentation. The sodium and potassium complexes with the TATP dimers can be seen in the spectrum at $m/z = 467$ and 483 , respectively.

potassium ion adducts of the TATP dimer at $m/z = 467$ and 483 , respectively. No monomer parent adduct ions were 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 has not dissociated upon deposition onto the surface. While the fragments of TATP can not be uniquely identified using our linear TOF instrument, a list of proposed structures consistent with fragment masses is included in the supporting material (Table S1). Finally, we note that the rich fragmentation spectrum presented in Figure 5 serves as a fingerprint for the TATP explosive.

CONCLUSION

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 mass spectrometry provides a new method to detect pure explosives on surfaces and formulations of explosives in the solid state. This method circumvents the limitations due to low vapor pressure 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 electrospray ionization and detected using time of flight mass spectrometry. The current sensitivity of LEMS for explosives is ~ 8 ng using a linear time-of-flight analyzer.

ACKNOWLEDGEMENTS

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SUPPORTING INFORMATION

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

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Figure Captions

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