# Determination of Inorganic Improvised Explosive Device Signatures Using Laser Electrospray Mass Spectrometry Detection with Offline Classification

Paul M. Flanigan, IV, John J. Brady, Elizabeth J. Judge, and Robert J. Levis*

Department of Chemistry and Center for Advanced Photonics Research, Temple University, 1901 N. 13th Street, Philadelphia, Pennsylvania 19122, United States

S *Supporting Information*

ABSTRACT: The mass spectral detection of low vapor pressure, inorganic-based explosive signatures including ammonium nitrate, chlorate, perchlorate, sugar, and the constituents contained within black powder are reported using laser electrospray mass spectrometry. The ambient pressure mass spectrometry technique combining nonresonant, femtosecond laser vaporization with electrospray postionization revealed primary and secondary signatures for trace quantities of inorganic explosives. A mixture of complexation agents in the electrospray solvent enabled the simultaneous detection of vaporized cations, anions, and neutrals in a single measurement. An offline classifier discriminated the inorganic-based explosives based on the mass spectral signatures resulting in high fidelity identification.
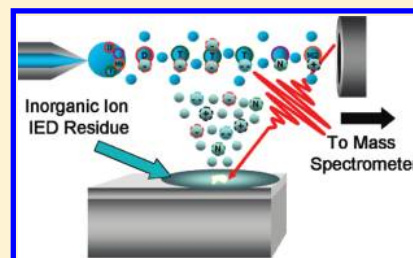
The ability to detect neutral, cationic, and anionic inorganic compounds with a wide range of vapor pressures is a challenging task. The difficulties are amplified when trace quantities are available and are dispersed on "real world" surfaces including glass, metal, plastic, wood, soil, or sand. Such an analytical challenge is present in the case of inorganic-based improvised explosives. Improvised explosive devices (IEDs) have been extensively used in criminal and terrorist attacks, as well as in asymmetric warfare. Explosives fall into two main classes ranging from high explosives, including unstable peroxides (TATP and HMTD) and nitrated organics (RDX, HMX, TNT, and PETN), to low explosives containing strong inorganic ion oxidizers, such as nitrates, chlorates, and perchlorates.[1,2] Due to the wide variability of constituents (i.e., explosives) contained in IEDs, the ability to detect broad classes of explosive signatures with a single instrument is significant.

Many techniques have the ability to detect high explosives, including ion mobility spectrometry (IMS),[3−5] gas chromatography (GC), high performance liquid chromatography (HPLC),[6] ion chromatography (IC),[7] capillary electrophoresis (CE),[8,9] laser-induced breakdown spectroscopy (LIBS),[10] and mass spectrometry (MS). Various ionization techniques coupled to MS have also successfully enabled the detection of high explosives, such as electrospray ionization (ESI),[11,12] atmospheric pressure chemical ionization (APCI),[13] desorption electrospray ionization (DESI),[14,15] direct analysis in real time (DART),[16] and laser desorption methods[17] including laser electrospray mass spectrometry (LEMS).[18] While mass spectrometry is an information rich technique and is on the rise for trace detection of nitrated and peroxide explosives, IMS is currently the method of choice for detection of explosives because of portability and commercial availability.[2,19]

Although there are many studies concerning the detection of high explosives, there have been considerably fewer investigations concerning the inorganic ion class of explosives. The major components of inorganic explosives are inorganic oxidizers, such as nitrates, chlorates, and perchlorates, and fuels, such as fuel oil, charcoal, sulfur, sugar, and metals (e.g., aluminum, magnesium, and zinc).[1] Other components commonly found in explosive formulations include gums, thickeners, and cross-linking agents. The most common inorganic ion IEDs include chlorates, perchlorates, ammonium nitrate, urea nitrate, black powder, and black powder derivatives (e.g., smokeless powders). The main analytical methods used for analysis of inorganic explosives are IC[1,7,20−22] and CE.[9,20,23,24] Also used, but not as often as IC and CE, are IMS, X-ray powder diffraction, spot tests, and mass spectrometric techniques, such as ESI-MS[13,25−27] and APCI-MS.[26] Although CE and IC are the chief methods for detecting the constituents contained within inorganic-based IEDs, both are separation methods requiring sample preparation (e.g., swabbing and elution) and analysis times ranging from approximately 5 to 20 minutes, respectively. In addition, analyzing cations and anions concurrently with IC requires either two separate columns or a zwitterionic column.[28] Dual detection of both cations and anions with CE entails two separate analyses, modification of the instrumentation, or alteration (via suppression or reversal) of the electro-osmotic flow through the use of surfactants.[23,29] Ideally, a technique well-suited for the identification of inorganic IED residues would be capable of analyzing cations and anions

simultaneously, without extensive sample preparation, and in the shortest possible time.

Laser electrospray mass spectrometry, a recently introduced laser-based ambient mass spectrometric technique, employs a nonresonant, femtosecond (fs) laser for vaporization of non-volatile samples and an electrospray ionization source for post-ionization. The femtosecond laser pulse vaporizes the sample material without the necessity of a resonant transition in the sample or a matrix. Nonresonant absorption of the radiation is enabled by the high intensity of the laser pulse (10^{13} W/cm^2). The ESI plume captures and ionizes the gas phase analytes and transfers the ionized molecules into the mass spectrometer for mass analysis. LEMS can directly analyze a surface at atmospheric pressure with no sample preparation steps required. Nonreso-nant femtosecond vaporization with electrospray ionization enables analysis of a variety of analytes including small[30] and large[31] biomolecules, narcotics,[32] pharmaceuticals, lipids,[33] pro-teins, and tissue.[34] In addition, high explosives, such as RDX, TATP, HMTD, and a propellant, were vaporized intact and mass analyzed using this method.[18] The goal of this study is to investigate the use of laser electrospray mass spectrometry for the detection of signatures from residues of postblast inorganic-based IEDs.

In any electrospray-based analysis technique, the bias applied to the ion optics typically dictates whether cations or anions will be detected. Simultaneous detection of both cations and anions in positive ion mode can be enabled through the use of pairing agents to yield complexes with overall positive charges, as first demonstrated for perchlorate detection using ESI-MS.[35] Complexation with cationic ion pairing agents enables detection of monovalent,[36,37] divalent,[38,39] and trivalent[40] anions in posi-tive ion mode electrospray. Two commercially available cationic pairing agents are investigated here for complexation of the anionic species in this study.

Additives to the electrospray solvent have additional value by translating inorganic cations out of the low m/z cutoff range for certain mass spectrometers[41,42] and out of regions of high background noise via chemical complexation. Lipids,[43] crown ethers,[44] and other compounds[45] can be used as hosts to allow for cation detection in the event that the mass spectrometer has a low mass cutoff. A lipid was examined in this experiment for translation of cations out of the low m/z cutoff region of the mass spectrometer for detection.

Here, we present the use of LEMS with an optimized electro-spray complexation solution consisting of two cationic pairing agents, a lipid and sodium acetate, to simultaneously detect cationic, anionic, and neutral analytes commonly observed in postblast inorganic-based IEDs. We investigate whether the mass spectra from residue of the various inorganic-based signatures seen in IEDs can be used to determine IED composition. Finally, we present principal component analysis (PCA) with linear discriminant analysis (LDA) to classify the explosive signatures.

■ EXPERIMENTAL SECTION

Materials. Cationic ion pairing agent solutions of 1,9-non-anediyl-bis(3-methylimidazolium) difluoride (D^{2+}) and 1,3-bis-[6-(3-benzyl-1-imidazolio)-hexyl]imidazolium trifluoride (T^{3+}) were purchased from Fluka Analytical (Sigma Aldrich, St. Louis, MO). The solid lipid sample of 1-monooleoyl-ra-glycerol (monoolein, MO) was purchased from MP Biomedicals (Solon, OH). The structures of the above binding agents are shown in

Figure S-1. All chemicals and reagents were of analytical grade from Fisher Scientific (Pittsburgh, PA) unless otherwise specified. Stock solutions of the following reagents were prepared in plastic containers at a concentration of 1×10^{-2} M using deionized water (≥ 18 MΩ cm) processed by a Millipore system (Millipore, Bedford, MA): sucrose, NaClO$_3$ (Sigma Aldrich), KClO$_4$ (Sigma Aldrich), KCl, NaCl, NH$_4$NO$_3$, NH$_4$Cl, KSCN, KOCN, Na$_2$S (Sigma Aldrich), NaHCO$_3$, CaCl$_2$, MgSO$_4$, NaS$_2$O$_3$, NaC$_2$H$_3$O$_2$ (sodium acetate, NaOAc), LiCl, RbCl, MgCl, and KNO$_3$.

Sample Preparation. A chlorate, perchlorate, and sugar (CPS) IED, an ammonium nitrate (AN) IED and a postblast black powder (BP$_{post}$) IED were simulated using the reagents from the stock solutions. The characteristic ions for each respective simulated IED were diluted into mixtures from the stock solutions with HPLC grade methanol (EMD Chemicals, Gibbstown, NJ) to a final concentration of 5×10^{-4} M. Black powder pellets were ground with a mortar and pestle and diluted with methanol to imitate a preblast black powder (BP) IED. A 15 μL aliquot was pipetted onto a 7 mm × 7 mm stainless steel sample plate and allowed to dry. The procedure was repeated three times for multiple sample slides, resulting in 45 μL and 22.5 nmol of each analyte deposited onto each slide. A preblast sample from a firework (purchased locally) was diluted into methanol and spotted on metal sample plates similar to the simulated IEDs. Postblast residue ejected from the firework after ignition was collected on multiple stainless steel plates (2.2 cm × 3.8 cm), which were placed in front of the firework at regular intervals (see Figure S-2 in Supporting Information). The plates were then analyzed using LEMS after removal of the remaining charcoal via compressed air.

The electrospray solvent mixture for the characterization of IEDs was prepared in a plastic syringe and consisted of 10 μM D^{2+}, 10 μM T^{3+}, 20 μM NaOAc, and 20 μM MO in 1:1 (v/v) water/methanol, in which the water was from Omnisolv High Purity HPLC grade water (EMD Chemicals).

Mass Spectrometry. The mass spectrometer used in this experiment has been previously described.[18,30−34] The system combines a femtosecond laser for the nonresonant transfer of analytes into the gas phase with an electrospray ion source for capture and ionization of the vaporized material. The electrospray ionization source (Analytica of Branford, Inc., Branford, CT) was operated in a configuration to produce positive ions. The ESI source utilizes an electrospray needle, dielectric capillary, skim-mer, and hexapole. The electrospray needle was maintained at ground while the inlet capillary was biased to −5.5 kV to perform positive ion mode ESI. The ESI needle was 6.4 mm above, and parallel to, the sample stage and was approximately 6.4 mm in front of the capillary entrance. The electrospray solvent mixture was pumped through the needle at a flow rate of 3 μL/min as set by the syringe pump (Harvard Apparatus, Holliston, MA). The ESI plume was dried by countercurrent nitrogen gas at 180 °C before entering the inlet capillary. The hexapole was operated in the trapping mode, where the positive ions were collected at 10 Hz. After exiting the ESI source, the ions were transferred to the extraction region by a second hexapole where they were injected orthogonally into the linear time-of-flight analyzer and extracted via two high voltage pulsers (Directed Energy Inc., Fort Collins, CO, and Quantum Technology Inc., Lake Mary, FL) triggered 50 μs after the ions exit the first hexapole. The positive ions were then detected, and the resulting mass spectra were averaged using a digital oscilloscope for 50 laser shots (5 s) for LEMS analysis and for 20 s for conventional ESI-MS analysis.

Table 1. Inorganic Ion IEDs and Their Constituents Analyzed in These Experiments

inorganic ion IED	cations	anions	neutrals
chlorate, perchlorate, sugar (CPS)	K^+, Na^+	Cl^-, ClO_3^-, ClO_4^-	sucrose
ammonium nitrate (AN)	NH_4^+	NO_3^-	N/A
preblast black powder (BP) (actual)	K^+	NO_3^-	sulfur, carbon
postblast black powder (BP_{post}) (simulated)	K^+, NH_4^+, Na^+, Mg^{2+}	NO_3^-, SCN^-, OCN^-, HCO_3^-, SO_4^{2-}, $S_2O_3^{2-}$, S^{2-}	N/A

N/A = Not Applicable

Laser Vaporization and Ionization. A Ti:sapphire laser oscillator (KM Laboratories, Inc., Boulder, CO) seeded a regenerative amplifier (Coherent, Inc., Santa Clara, CA) to create a 2.5 mJ pulse centered at 800 nm with a duration of 70 fs, operating at 10 Hz to couple with the electrospray ion source. The laser was focused to a spot size of ~400 μm in diameter using a 16.9 cm focal length lens, with an incident angle of 45° with respect to the sample. The intensity of the laser at the substrate was approximately 2×10^{13} W/cm^2. The steel sample plate was biased to −2.0 kV to compensate for the distortion of the electric field between the capillary and the needle caused by the sample stage. The area sampled was 6.4 mm below and 1 mm in front of the electrospray needle. The sample was ejected in a direction perpendicular to the electrospray plume, where capture and ionization occurred. An ESI solvent background mass spectrum was acquired before vaporization of each sample set to allow background subtraction of solvent and pairing agent-related peaks. Large negative features can result in the blank-subtracted mass spectra because of the vaporized analytes altering the solvent ion distribution due to the competition of the analytes, pairing agents, and solvent for charge. Positive peaks not labeled in the blank-subtracted mass spectra are solvent-related features.

Limit of Detection for Ammonium Nitrate. The limit of detection (LOD) for the inorganic ion detection system was determined for ammonium nitrate (NH_4NO_3) by comparing the acquired mass spectra from LEMS and conventional ESI-MS experiments. First, the LEMS measurement involved vaporizing ammonium nitrate from a metal slide after deposition and drying of three, 15 μL aliquots (45 μL total) of a solution with varying molarity, 10 μM to 5 mM. The vaporized sample was captured and ionized by the electrospray solvent containing D^{2+}, T^{3+}, MO, and NaOAc. For each sample concentration, at least 10 mass spectra were acquired and averaged, in which each spectrum consisted of the average signal resulting from 50 laser shots. Conventional ESI-MS data was acquired by electrospraying the solution of the pairing agents and NH_4NO_3 of varying molarity (10 μM to 1 mM). Three mass spectra, each consisting of 20 s averages, were collected for the ESI mass spectra measurements. The peaks of interest were integrated using the Cutter program.[46]

Safety Considerations. Appropriate laser eye protection was worn by all lab personnel.

■ RESULTS AND DISCUSSION

Nonresonant Vaporization of Chlorate, Perchlorate, Sugar and Ammonium Nitrate IEDs. Chlorate, perchlorate, and sugar-based IEDs pose a challenge for mass spectrometry due to the extremely low vapor pressure of the compounds in the formulation. Nonresonant laser vaporization was employed to transfer the CPS compounds into the gas phase for subsequent ionization using an optimized electrospray solvent to determine whether complexation would occur between the pairing agents and the vaporized residue. Table 1 lists the target analytes of the simulated inorganic ion IEDs tested in this experiment. The analytes for the CPS mixture included sodium, potassium, chlorate, perchlorate, chloride, and sucrose. The mass spectrum for the CPS mixture, Figure 1a, reveals that the T^{3+} pairing agent binds singly charged anions, complexing with chloride, chlorate, and perchlorate yielding the ions $[T^{3+} + Cl^-]^{2+}$ at m/z 293, $[T^{3+} + ClO_3^-]^{2+}$ at 318, and $[T^{3+} + ClO_4^-]^{2+}$ at 325, respectively. The D^{2+} pairing agent, which only binds with monovalent anions, complexes with perchlorate at m/z 389 ($[D^{2+} + ClO_4^-]^+$). Although chloride and chlorate should also complex with D^{2+}, these features are not distinguished in the mass spectrum as the chloride peak is obscured by the $[T^{3+} + ClO_4^-]^{2+}$ feature at m/z 325 while the solvent background may hide the chlorate feature at m/z 373. Chloride-containing anion—T^{3+} complexes (at m/z 293, 318, and 325) do not show the typical 3:1 mass spectral intensities from the isotopic ratio of chloride, whereas complexes with D^{2+} show these isotopic features (seen at m/z 389 for the perchlorate complex). This is due to the higher charge state of the doubly charged T^{3+} complexes, which reduces the difference of the isotopic mass spectral features from 2 to 1 m/z units, which is not resolvable with the current mass spectrometer configuration. In general, T^{3+} has a higher affinity for most of the monovalent anions than D^{2+}, on the basis of control measurements of the complexes. This trend is consistent with previous complexation measurements for five organic monovalent acids.[38] Peaks corresponding to m/z higher than 500 often correspond to T^{3+} complexes with either a doubly charged anion or two singly charged anions. The measurements for CPS reveal characteristic peaks at m/z 559, 734, and 751. The feature at m/z 559 represents an unidentified reaction product and is unique to the simulated CPS IED. The peaks at m/z 734 and 751 represent complexes of T^{3+} with two singly charged anions, $[T^{3+} + ClO_3^- + ClO_4^-]^+$ and $[T^{3+} + 2ClO_4^-]^+$, respectively. The assignments of all mass spectral features used for identification for this IED and others are listed in Table 2.

In the electrospray ionization process, cationic adducts enable the detection of neutral analytes. Sodium acetate was included in the electrospray solution to investigate the possibility of Na^+ complexing to neutrals, resulting in a $[M + Na^+]^+$ ion. The feature at m/z 365 in Figure 1a is consistent with sucrose plus a sodium adduct. Acetate does not interfere with the mass spectral analysis as the acetate anion has a low affinity for D^{2+} as exhibited by its high LOD.[36] The possible complexes resulting from acetate complexation with T^{3+} are not readily distinguishable in control mass spectra.

In the case of a low mass cutoff or mass spectral congestion, molecules such as lipids or crown ethers permit the detection of low mass cations due to cationic adduct-complexes. Monoolein, a monoglyceride with one unsaturated site in the 18-hydrocarbon chain, was chosen to translate cationic mass spectral signatures
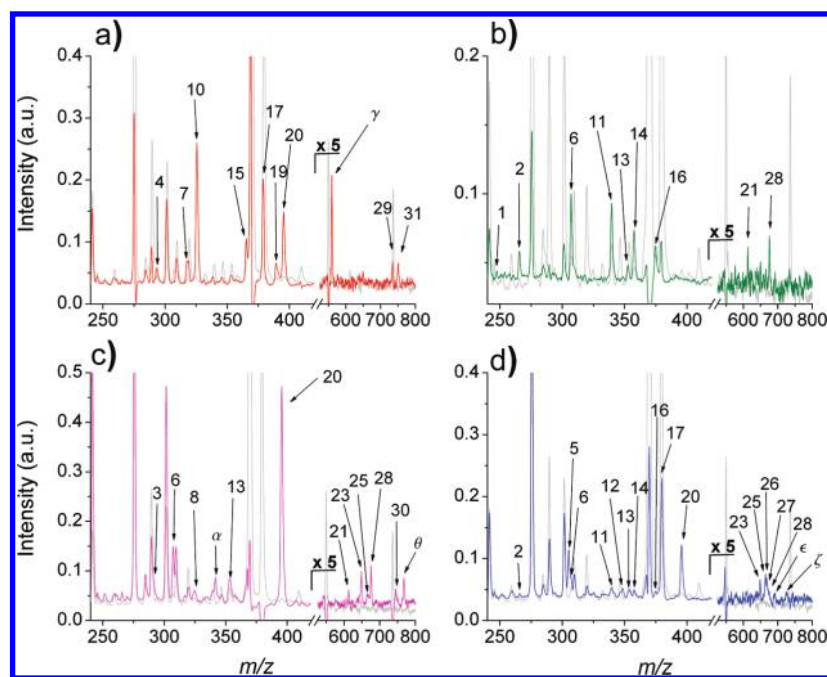
Figure 1. LEMS mass spectra (blank subtracted, with the blank spectra in gray) showing characteristic peaks for four inorganic explosive materials: (a) chlorate, perchlorate, and sugar (CPS), (b) ammonium nitrate (AN), (c) preblast black powder (BP), and (d) simulated, postblast black powder (BP$_{post}$). The features above m/z 500 are magnified 5×. Peaks are numbered for clarification (listed in Table 2). Unidentified peaks, labeled with Greek letters and corresponding m/z in parentheses, include α (342), γ (559), δ (609), ε (692), ζ (724), η (752), and θ (768).

Table 2. List of Complexes with Their Corresponding m/z Value^{a}

peak number	m/z	corresponds to	peak number	m/z	corresponds to
1	247	$[RCO - H_2O]^+$	17	380	$[MO + Na^+]^+$
2	265	$[RCO]^+$	18	387	$[D^{2+} + HSO_4^-]^+$
3	292	$[T^{3+} + HS^-]^{2+}$	19	389	$[D^{2+} + ClO_4^-]^+$
4	293	$[T^{3+} + Cl^-]^{2+}$	20	395	$[MO + K^+]^+$
5	305	$[T^{3+} + SCN^-]^{2+}$	21	613	$[T^{3+} + CO_3^{2-}]^+$
6	307	$[T^{3+} + NO_3^-]^{2+}$	22	645	$[T^{3+} + SCN^- + Cl^-]^+$
7	318	$[T^{3+} + ClO_3^-]^{2+}$	23	648	$[T^{3+} + SO_4^{2-}]^+$
8	324	$[T^{3+} + HSO_4^-]^{2+}$	24	649	$[T^{3+} + NO_3^- + Cl^-]^+$
9	325	$[D^{2+} + Cl^-]^+$	25	664	$[T^{3+} + S_2O_3^{2-}]^+$
10	326	$[T^{3+} + ClO_4^-]^{2+}$	26	668	$[T^{3+} + 2SCN^-]^+$
11	339	$[RCOO + C_3H_6O^+]^+$	27	672	$[T^{3+} + SCN^- + NO_3^-]^+$
12	348	$[D^{2+} + SCN^-]^+$	28	676	$[T^{3+} + 2NO_3^-]^+$
13	352	$[D^{2+} + NO_3^-]^+$	29	734	$[T^{3+} + ClO_3^- + ClO_4^-]^+$
14	357	$[MO + H^+]^+$	30	746	$[T^{3+} + 2HSO_4^-]^+$
15	365	$[Na^+ + sucrose]^+$	31	751	$[T^{3+} + 2ClO_4^-]^+$
16	375	$[MO + NH_4^+]^+$			

^{a} Abbreviations are as follows: D^{2+} = 1,9-nonanediyl-bis(3-methylimidazolium), T^{3+} = 1,3-bis[6-(3-benzyl-1-imidazolio)-hexyl]imidazolium, and MO = monoolein. RCO and RCOO correspond to fragments of monoolein, where the R represents the 17-hydrocarbon chain as denoted in Figure S-1.

out of the low m/z cutoff/high background signal range for subsequent detection. In the CPS mixture, potassium and sodium were the cationic species of interest. The mass spectral feature observed at m/z 395 represents the potassium adduct of MO. The sodium adduct of monoolein ion at m/z 380 is not readily distinguishable because of solvent interference from the use of sodium acetate in the optimized electrospray solvent.

Ammonium nitrate has been widely studied due to its extensive use in explosives (ANFO and other slurry-type explosives) and to

the relatively easy procurement or synthesis. The ESI-MS of nitrates (ammonium, sodium, and potassium) result in cluster ions that span a large m/z region for identification, and the distribution depends upon the heated capillary temperature.[13,25] Cluster ions are also observed during ESI-MS analysis of other oxidizers, such as chlorates and perchlorates.[27] Clusters from mixtures of oxidizers that often comprise an IED make identification arduous due to the enormous number of mass spectral features.[27] Although clusters from oxidizers were observed in

previous ESI-MS analyses, no cluster ions were identified for ammonium nitrate in the LEMS experiment, presumably due to the laser vaporization process, the temperature of the drying gas, and the presence of pairing agents. In this experiment, ammonium and nitrate were the sole analytes for the simulated ammonium nitrate IED. Figure 1b shows the mass spectrum for AN using LEMS. The AN mass spectrum has characteristic peaks at m/z 307, 352, 357, 374, and 676 that correspond to $[T^{3+} + NO_3^-]^{2+}$, $[D^{2+} + NO_3^-]^+$, $[MO + H^+]^+$, $[MO + NH_4^+]^+$ and $[T^{3+} + 2NO_3^-]^+$, respectively. In addition to complexes with ionic species, the AN spectrum reveals fragmented monoolein features, resulting from complexation with ammonium, that are observed at m/z 265 and 339. Such fragmentation is not observed under the same mass spectrometric conditions with other cationic species such as sodium, potassium, lithium, rubidium, magnesium, and calcium (Figures S-3 and S-4). Cationic ammonium adducts have been previously used with tandem MS to characterize lipids, revealing fragments (with m/z in parentheses) such as $[RCO - H_2O]^+$ (247), $[RCO]^+$ (265), and $[RCOO + C_3H_6O^+]^+$ (339).[43,47,48] These MO fragments are secondary signatures for the presence of the ammonium ion and can aid in the classification of inorganic ion IEDs. A multidimensional approach using all possible signature elements from the mixtures, including these secondary signatures, is important for discriminating unknown explosives.

Limit of Detection using Ammonium Nitrate. The LOD for IED characterization was determined through comparison of LEMS and conventional ESI-MS measurements of AN. The LEMS and conventional ESI-MS mass spectra of AN (Figure S-5 in Supporting Information) have the same mass spectral features as seen in Figure 1b, including multiple nitrate complexes, an ammonium adduct of monoolein, and several monoolein fragments. Calibration curves for ESI-MS and LEMS (Figures S-6 and S-7, respectively) were measured for the nitrate complex at m/z 307 ($[T^{3+} + NO_3^-]^{2+}$), the ammonium complex at m/z 374 ($[MO + NH_4^+]^+$), and the sum of the ammonium complex at m/z 374 with the monoolein-related peaks at m/z 247 ($[RCO - H_2O]^+$), 265 ($[RCO]^+$), 339 ($[RCOO + C_3H_6O^+]^+$) and protonated monoolein at m/z 357 ($[MO + H^+]^+$). The LOD values for the nitrate and ammonium signatures were calculated using the linear region from 0 to 100 μM for ESI-MS and 0 to 500 μM AN (0 to 1.8 μg deposited onto the sample plate) for LEMS. Note that there was no detectable signal using LEMS for the ammoniated monoolein at m/z 374 when the concentration deposited on the sample plate was less than 100 μM (360 ng total). Signal for the MO fragments was detected at concentrations less than 100 μM revealing that ammoniated monoolein yields secondary fragmentation signatures. The LOD for nitrate was calculated using the T^{3+} complex at m/z 307, which is more intense than the $[D^{2+} + NO_3^-]^+$ signal at 352 due to the varying binding efficiencies. At higher concentrations, the analyte—pairing agent complexes are saturated, which is typical for ESI-MS.[49]

A direct comparison of the LOD values between ESI-MS and LEMS reveals that ESI is approximately 2 orders of magnitude more sensitive than LEMS. For ESI-MS, the LOD was derived from the calibration curves (Figure S-6) and the volume delivered during analysis (1 μL to acquire 200 mass spectra). The LOD for conventional ESI-MS measurement was found to be 13 ± 2 pmol ($\sim$ 780 ± 120 pg) and 7 ± 0.7 pmol ($\sim$125 ± 10 pg) for nitrate and ammonium, respectively, as shown in Table S-1. For the LEMS measurement, the LOD was derived from the amount of analyte deposited on the sample plate and the 200 laser shots/

mass spectra per sample. The LOD using LEMS was 1.9 ± 0.8 nmol ($\sim$ 120 ± 50 ng) for nitrate and 2.8 ± 0.7 nmol ($\sim$ 50 ± 12 ng) for ammonium. Inorganic ion analyses performed with IC[22] and CE[24] are several orders of magnitude more sensitive than LEMS with LODs in the picomole to femtomole range. The higher LOD values for LEMS result from the low neutral capture efficiency of the vaporized analytes by the electrospray[32] and nonequilibrium binding kinetics. The LOD for other ions will differ due to varying binding/complexation efficiencies with the pairing agents. Chemical adsorption to surfaces other than stainless steel, such as glass, wood, or fabrics, may contribute to a slight decrease in sensitivity in LEMS analyses, as seen previously for other analytes.[32] In addition, these LOD values are not necessarily the limits of detection for femtosecond laser vaporization with electrospray postionization, given the sensitivity of the home-built mass spectrometer. ESI-MS measurements were slightly more reproducible than LEMS measurements (as seen in Table S-2). Higher relative standard deviations (RSDs) for LEMS data is not due to laser fluctuations, but due to inhomogeneity inherent in the dried droplet technique, which has been seen in previous LEMS[33] and MALDI experiments.[50]

Nonresonant Vaporization of Black Powder and Simulated Postblast Black Powder. Detection of black powder is important because of commercial availability. Black powder primarily consists of potassium nitrate mixed with sulfur and carbon in the form of charcoal.[51] Figure 1c represents the mass spectrum resulting from LEMS analysis of the crushed black powder IED, showing features at m/z 292, 307, 324, 342, 352, 394, 648, 676, 746, and 768. Table 2 lists the pairing agent—inorganic ion complexes with their corresponding m/z used for identification of features in the mass spectra. Only complexes of potassium ($[MO + K^+]^+$ at m/z 394), nitrate ($[T^{3+} + NO_3^-]^{2+}$ at m/z 307, $[D^{2+} + NO_3^-]^+$ at 352, and $[T^{3+} + 2NO_3^-]^+$ at 676), and sulfur-related ions ($[T^{3+} + HS^-]^{2+}$ at m/z 292, $[T^{3+} + HSO_4^-]^{2+}$ at 324, $[T^{3+} + SO_4^{2-}]^+$ at 648, and $[T^{3+} + 2HSO_4^-]^+$ at 746) were seen in the BP IED mass spectrum, in accord with the composition of the IED. T^{3+} complexes not only with singly charged anions, but also with doubly charged anions, as seen in the complexation with sulfate at m/z 648. A feature observed at m/z 342 was not identified (due to the lack of MS^n) but was correlated with the black powder samples.

Postblast black powder consists of a mixture of salts that can provide an information rich mass spectrum. Multidimensional analysis is necessary for discrimination of such a complex mass spectrum. Potential analytes for simulated postblast black powder IED include sodium, potassium, ammonium, magnesium, nitrate, sulfate, thiosulfate, sulfide, cyanate, thiocyanate, and bicarbonate. The mass spectrum of the mixture of these compounds is shown in Figure 1d and has characteristic peaks at m/z 305, 307, 348, 352, 374, 395, 648, 664, 668, 672, and 676. Thiocyanate (SCN$^-$) complexes with D^{2+} and T^{3+} to yield the ions $[D^{2+} + SCN^-]^+$, $[T^{3+} + SCN^-]^{2+}$, $[T^{3+} + 2SCN^-]^+$, and $[T^{3+} + SCN^- + NO_3^-]^+$ at m/z 348, 305, 668, and 672, respectively. In addition, nitrate complexes with T^{3+} and D^{2+} to yield ions at m/z 307 ($[T^{3+} + NO_3^-]^{2+}$), 352 ($[D^{2+} + NO_3^-]^+$), and 676 ($[T^{3+} + 2NO_3^-]^+$). Cationic adducts of monoolein are observed at m/z 357 (H$^+$), 374 (NH$_4^+$), 380 (Na$^+$), and 395 (K$^+$). One monoolein fragment peak is observed in the mass spectrum at m/z 339 ($[RCOO + C_3H_6O^+]^+$). The MO-fragment features are minor compared to those in the AN spectrum due to the reduced amount of ammoniated monoolein, resulting
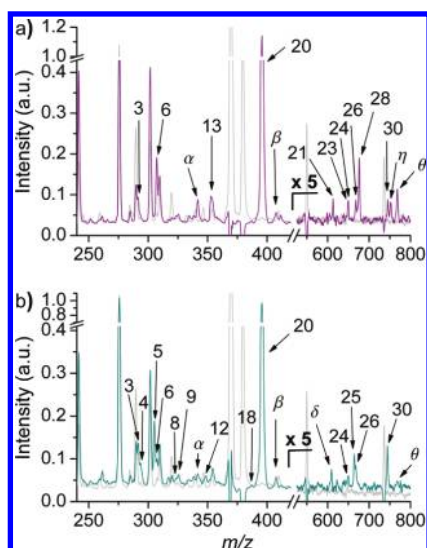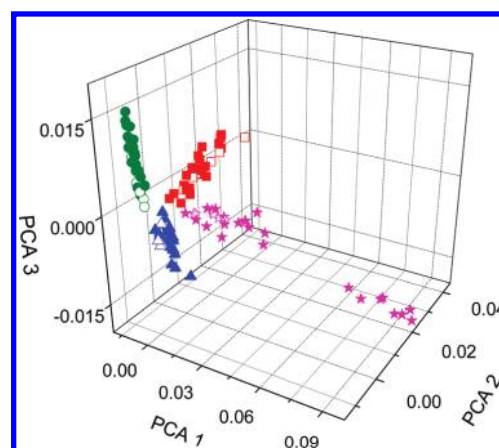
Figure 2. LEMS mass spectra (blank subtracted, with blank in gray) showing signature features for (a) preblast firework residue and (b) postblast firework residue. The features above m/z 500 are magnified $5\times$. Peaks are numbered for clarification (listed in Table 2). Unidentified peaks, labeled with Greek letters and corresponding m/z in parentheses, include α (342), β (407), γ (559), δ (609), η (752), and θ (768).

Figure 3. PCA analysis projected into three of the six dimensions for chlorate, perchlorate, and sugar (red ■); ammonium nitrate (green ●); preblast black powder (magenta ★); and simulated, postblast black powder (blue ▲) IEDs showing separation among the four simulated inorganic-based IEDs. The open symbols (□, ○, ☆, and △) and the filled, colored symbols (■, ●, ★, and ▲) represent the training and testing sets for each IED, respectively.

from multiple cations competing for MO complexation. The doubly charged anions sulfate (SO_4^{2-}) and thiosulfate ($S_2O_3^{2-}$) bind exclusively to T^{3+} yielding singly charged complexes at m/z 648 and 664, respectively. Although included in the BP_{post} solution, cyanate (OCN^-) and sulfide (S^{2-}) were not identified in the mass spectrum due to small binding efficiencies,[36,39] ion competition, and ion suppression effects.[49,52] No identifiable feature was assigned for magnesium, the only doubly charged cation included in this study, presumably because of a low binding efficiency with MO.

Analysis of Preblast and Postblast Fireworks. To determine whether LEMS could distinguish very similar inorganic IEDs from actual samples, residue from a commercial firework was examined in two different forms, preblast and postblast. The resulting mass spectra obtained from the analyses of preblast and postblast residue are shown in Figure 2. The preblast and postblast spectra both have peaks at m/z 292 ($[T^{3+} + HS^-]^{2+}$), 307 ($[T^{3+} + NO_3^-]^{2+}$), 342 (unidentified but unique to black powder samples), 394 ($[MO + K^+]^+$), 649 ($[T^{3+} + Cl^- + NO_3^-]^+$), and 668 ($[T^{3+} + 2SCN^-]^+$). However, there are some differences in the obtained mass spectra. The preblast residue mass spectrum contains more nitrate and potassium, as shown by the higher ion abundances at m/z 307 and 394, respectively. In addition, there are several features that are not observed in the postblast spectrum, including peaks at m/z 352 ($[D^{2+} + NO_3^-]^+$) and 676 ($[T^{3+} + 2NO_3^-]^+$). The postblast mass spectrum consists of unique ions such as chloride, thiocyanate, and thiosulfate at m/z 293 ($[T^{3+} + Cl^-]^{2+}$), 305 ($[T^{3+} + SCN^-]^{2+}$), 348 ($[D^{2+} + SCN^-]^+$), and 664 ($T^{3+} + S_2O_3^{2-}]^+$), respectively.

Classification of Inorganic IEDs. The group of target analytes includes many species that may be present in the background including cations such as potassium, sodium, magnesium, and calcium and anions such as nitrate, sulfate, and carbonate that are abundant on many surfaces and/or in the

atmosphere. Background contaminants increase the difficulty for classifying these samples. A false positive could occur solely based on the appearance of only one of these cations or anions in the mass spectrum. For instance, relying only on either ammonium or nitrate ions for identification of an ammonium nitrate IED could result in misclassification. However, having multiple signatures for an inorganic-based IED reduces the probability of false positives or false negatives, suggesting the value of multidimensional analysis.

LEMS, in combination with an optimized electrospray solvent, allows for rapid multidimensional analysis of cations and anions simultaneously from inorganic IEDs, facilitating accurate identification. Four explosive formulations, as shown in Figure 1, were investigated to evaluate the potential for IED classification using LEMS. To determine whether mass spectral features from LEMS analyses can be used to discriminate inorganic explosives, a library of 40 characteristic peaks was created. These 40 features were integrated for 24 mass spectra (6 mass spectra for each of the 4 distinct inorganic IEDs) yielding a 24×40 matrix. This training set was then subjected to principal component analysis (PCA) in Matlab, yielding the transformed data set [mean-adjusted training set (24×40 matrix) times the calculated eigenvectors (40×40 matrix)]. The eigenvectors resulting from the PCA of the training set were then multiplied by the remaining mean-adjusted data contained in the testing data set (24 integrated mass spectra from each IED, resulting in a 96×40 matrix). Classification of the testing data was performed using linear discriminant analysis (LDA) via Matlab software. Figure 3 shows the projection of the training and testing data using three of the six principal components for the inorganic materials. The training set is denoted by the unfilled symbols. As can be seen, the principal components cluster the explosives well, allowing for accurate classification.

The inorganic test set (Table 3) was classified with high fidelity. All of the mass spectra were classified correctly with the exception of a single sample of the CPS IED. A 99% accuracy was obtained for the classification of all IED compounds. If nearest neighbor classification is used, 100% discrimination of all

Table 3. Classification of Inorganic Ion IEDs Using PCA with LDA Analysis

inorganic ion IED	training set size	samples correctly characterized	percentage
chlorate, perchlorate, sugar	6	23/24	96%
ammonium nitrate	6	24/24	100%
preblast black powder (actual)	6	24/24	100%
postblast black powder (simulated)	6	24/24	100%
total	24	95/96	99%

samples could be achieved. However, LDA was used as it is the most commonly used classifier. The clear separation of the inorganic IEDs in three-dimensional detection space and the correct classification using a training set demonstrates that inorganic ion IED samples can be discriminated using PCA with LDA.

■ CONCLUSION

The ability to detect all classes of explosives with a single instrument is of great significance at the current time. The detection of inorganic-based improvised explosives is difficult due to the need for a method capable of analyzing cations, anions, and neutral analytes simultaneously with possible background contamination. We demonstrated that LEMS is capable of rapid mass analysis of trace amounts of inorganic-based explosives directly from a metallic surface. The nonresonant femtosecond laser vaporizes low vapor pressure inorganic analytes into the gas phase where they bind to complexation agents in the electrosprayed solvent, allowing for simultaneous mass analysis of cationic, anionic, and neutral species. The mass spectrum of an explosive provides multiple signatures, reducing the probability of false negatives or false positives in the identification and classification of these explosives. Using an offline classifier, these explosives were discriminated with high accuracy. The capability to detect inorganic-based explosives is a step toward universal LEMS analysis and classification of complex samples.

■ ASSOCIATED CONTENT

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

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rjlevis@temple.edu.

■ ACKNOWLEDGMENT

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