In-source collision induced dissociation of inorganic explosives for mass spectrometric signature detection and chemical imaging

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Abstract

The trace detection, bulk quantification, and chemical imaging of inorganic explosives and components was demonstrated utilizing in-source collision induced dissociation (CID) coupled with laser desorption/ionization mass spectrometry (LDI-MS). The incorporation of in-source CID provided direct control over the extent of adduct and cluster fragmentation as well as organic noise reduction for the enhanced detection of both the elemental and molecular ion signatures of fuel-oxidizer mixtures and other inorganic components of explosive devices. Investigation of oxidizer molecular anions, specifically, nitrates, chlorates, and perchlorates, identified that the optimal in-source CID existed at the transition between fragmentation of the ionic salt bonds and molecular anion bonds. The chemical imaging of oxidizer particles from

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4 latent fingerprints was demonstrated, including both cation and anion components in positive and
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6 negative mode mass spectrometry, respectively. This investigation demonstrated LDI-MS with
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8 in-source CID as a versatile tool for security fields, as well as environmental monitoring and
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10 nuclear safeguards, facilitating the detection of elemental and molecular inorganic compounds at
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12 nanogram levels.
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19 **KEYWORDS:** In-source collision induced dissociation; mass spectrometry; fuel-oxidizer
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21 mixtures; inorganic explosives; laser desorption/ionization; chemical imaging;
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30 **1. Introduction**

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33 Significant research has been conducted advancing the accurate and sensitive detection of
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35 explosives, most frequently common military-grade nitrated organic explosives, including
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37 nitramines, nitroaromatics, and nitrate esters such as cyclotrimethylenetrinitramine (RDX),
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39 trinitrotoluene (TNT), and pentaerythritol tetranitrate (PETN). These explosives have been
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41 detected using a range of analytical techniques, including ion chromatography (IC) [1, 2],
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43 capillary electrophoresis (CE) [3, 4], high performance liquid chromatography (HPLC) [5], and
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45 most notably, ion mobility spectrometry (IMS) [6-13] and mass spectrometry (MS) [14-22]. The
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47 rapid analysis times and cost effectiveness of these field compatible instruments have led to
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49 widespread deployment of ion mobility spectrometry. Nevertheless, developments in ambient
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51 and atmospheric pressure ionization mass spectrometry have provided selective and sensitive
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53 alternatives, including a range of analyte ionization techniques requiring no or minimal sample
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4 preparation such as desorption electrospray ionization (DESI) [23] and direct analysis in real
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6 time (DART) [24]. A number of reviews and books provide extensive details on the many
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8 ambient ionization techniques and specifics of explosives detection [25-30].
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11 The threats posed by homemade and improvised explosive devices (HMEs/IEDs)
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13 continue to increase, necessitating the growth of techniques for the trace detection of their widely
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15 varying signatures. These HMEs and IED components include unstable primary explosives (*e.g.*,
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17 peroxides [31-34], azides, and fulminates), fuel-oxidizer and self-initiating mixtures, nitrated
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19 sugar alcohols, and radiological dispersion devices (RDDs) [34-37]. In the present work, we
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21 focus on the detection of inorganic explosives and components, a rising area of research. Fuel-
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23 oxidizer mixtures may contain both organic (*e.g.*, fuel-oil, sugar, or nitromethane) and inorganic
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25 (*e.g.*, potassium chlorate, ammonium nitrate, or aluminum) components. Evans-Nguyen *et al.*
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27 [35] and Forbes and Sisco [34] recently demonstrated enhanced detection of elemental inorganic
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29 components of explosives/explosive devices using in-source collision induced dissociation (CID)
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31 combined with liquid based ambient ionization sources, transmission mode desorption
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33 electrospray ionization (TM-DESI) and desorption electro-flow focusing ionization (DEFFI).
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35 The incorporation of in-source CID led to 10-fold to 100-fold improvements in detection of
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37 elemental inorganic ions by increasing fragmentation of adducts and clusters formed by
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39 inorganic compounds and decreasing chemical noise from organic compounds [34, 35, 38]. In
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41 addition, tuning of in-source CID has enabled control over charge reduction from the doubly
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43 charged to singly charged cations of alkaline earth metal ions [38]. These previous studies
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45 utilized liquid-based ion sources and focused on how in-source CID affected the response of
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47 organic explosives and inorganic elemental components of explosives and explosive devices.
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49 The detection of inorganic particles was demonstrated by incorporating a 5 % nitric acid aqueous
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4 solution. However, to circumvent the need for nitric acid, we present an investigation of laser-
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6 based desorption and ionization of inorganic particles and residues. Here, we investigate the
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8 effects of in-source CID on the detection of inorganic explosives, both elemental and molecular,
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10 highlighting inorganic oxidizers.
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14 The analytical performance and detection optimization for inorganic explosives (*e.g.*,
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16 fuel-oxidizer mixtures) using in-source CID is presented. CID was investigated using a laser
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18 desorption/ionization mass spectrometry (LDI-MS) system. The integration of elevated in-source
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20 CID potentials led to increased ion acceleration and collisions with atmospheric gas molecules,
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22 relative to typical CID (declustering) potentials, in the mass spectrometer inlet region. These
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24 more frequent and higher energy collisions led to fragmentation of inorganic adducts and
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26 clusters. The characteristic in-source CID response for inorganic ions was dependent on the ion
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28 composition (*e.g.*, elemental: K^+ vs molecular: ClO_4^-) as well as the originating salt composition
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30 (*e.g.*, ammonium nitrate vs potassium nitrate). The optimized detection of inorganic explosive
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32 components was then used to demonstrate the direct detection of oxidizer particles from a
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34 complex matrix (*i.e.*, latent fingerprints), bulk quantification from extracted collection regions
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36 that included both inorganic and organic components, and chemical imaging of particles from
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38 latent fingerprints.
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46 47 **2. Experimental Methods**

48 49 50 **2.1 Materials and Sample Preparation**

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53 Salts (potassium chlorate: PC, potassium perchlorate: PPC, potassium nitrate: PN,
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55 ammonium nitrate: AN, and calcium ammonium nitrate: CAN) and metals (zinc, aluminum,
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57 magnesium, strontium, and cobalt) were purchased from Sigma Aldrich (St. Louis, MO) and
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4 Inorganic Ventures (Christiansburg, VA), respectively.* The salts were either crushed with a
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6 metal spatula for direct particle analysis or dissolved in water and diluted to required
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8 concentrations for parametric analyses. Similarly, ICP-MS standards from Inorganic Ventures
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10 were purchased at 1 mg mL⁻¹ in an aqueous solution with 0.1 % to 3 % nitric acid (vol/vol) and
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12 further diluted as required. Liquid chromatography-mass spectrometry (LC-MS) Ultra
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14 Chromasolv® grade water was purchased from Sigma Aldrich (St. Louis, MO) and used for all
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16 sample preparation. Parametric investigations and chemical imaging were conducted on LDI
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18 commercial substrates from Hudson Surface Technology (Old Tappan, NJ). Solution aliquots of
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20 1 µL of each analyte concentration (500 pg µL⁻¹ to 1 µg µL⁻¹, depending on the experiment) were
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22 spotted onto the patterned LDI substrates (PSU0106000: µFocus MALDI Plate). Direct detection
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24 and chemical imaging of complex matrices were conducted from latent fingerprints deposited by
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26 an anonymous volunteer directly onto a blank LDI substrate (PSG0103000: NonFocus HST
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28 Array for Imaging). Latent fingerprints were collected per NIST Institutional Review Board Case
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30 407 protocol and no volunteers handled or were exposed to exogenous inorganic chemicals.
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33 Fingerprint deposition and collection was followed by the dry transfer of particles of relevant
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35 inorganic oxidizer onto the latent fingerprint. Explosive residues generated during a homemade
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37 material synthesis of a simulated explosive device were collected on adhesive sheets (samples
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39 provided by Signature Science, Charlottesville, VA). Three individual samples were collected
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41 from a fuel-oxidizer mixture synthesis containing potassium perchlorate and icing sugar. Each 15
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43 mm × 20 mm sample section of the adhesive sheet, containing collected inorganic and organic
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45 compounds, was placed into a 5 mL vial and extracted into 2 mL of water, mixed for ten minutes
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47 on a rotating mixer at 20 rpm, and then vortexed for 60 s. Standards for linear least squares
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49 calibration were prepared gravimetrically using milligram quantities of crystalline salt analytes
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with manufacturer designated purities of $\geq 99.0\%$ (AT21 comparator balance, Mettler Toledo, Columbus, OH). Nominal solution concentrations of 1 mg mL^{-1} were prepared and gravimetrically diluted.

* Certain commercial products are identified in order to adequately specify the procedure; this does not imply endorsement or recommendation by NIST, nor does it imply that such products are necessarily the best available for the purpose.

2.2 Instrumentation

2.2.1 Mass Analyzer and Imaging

A 4000 QTrap MS/MS system, consisting of a hybrid triple quadrupole/linear ion trap, (Applied Biosystems/MDS Sciex, Foster City, CA/Toronto, Canada) and a 35 mm extended capillary heated interface was used in this experiment (Figure 1), with additional details of the instrument parameters and operation found in the literature [20, 39]. Briefly, experiments included the following system parameters: 138 kPa curtain gas (N_2), 83 kPa ion source gas 1 (N_2), 0.0 kPa ion source gas 2 (N_2), 100 °C interface temperature, $\pm 10\text{ V}$ entrance potential, and $1.1 \times 10^{-3}\text{ kPa}$ to $1.3 \times 10^{-3}\text{ kPa}$ operating vacuum. In-source CID of various analyte adducts/clusters and organic compounds was achieved at the instrument orifice, between the curtain plate and skimmer cone (Figure 1). The extent of CID was manipulated through the instrument's declustering potential in the differentially pumped region. Principally, the characterization of in-source CID of inorganic explosives was conducted utilizing the first quadrupole for mass analysis and the remaining quadrupoles as ion guides. In-source CID potentials were varied from $\pm 25\text{ V}$ to $\pm 375\text{ V}$ for positive and negative mode experiments. Samples were interrogated across a specified m/z window for 5 s at each CID potential interval. Tandem mass spectrometry (MS/MS) product ion scans were used for the identification of

various adducts/clusters and the characterization of molecular ion fragmentation. Here, a specific mass of interest was selected by the first quadrupole, fragmented by the second quadrupole, and scanned by the third quadrupole. The laser desorption/ionization source (details below) was synchronized with the instrument and data acquisition software for mass spectrometry imaging (MSI) experiments. Details of peripheral device synchronization can be found in the literature [39]. Chemical image data was collected from 5 mm $\times$ 5 mm regions of interest divided into 100 $\mu\text{m} \times 100 \mu\text{m}$ pixels and scanned at a constant 12.5 mm/min velocity in a unidirectional pattern. Imaging and image analysis of the mass spectrometric data was completed with MSiReader, a MATLAB-based freeware package (v0.04, W. M. Keck FT-ICR Mass Spectrometry Laboratory, North Carolina State University) [40].

2.2.2 Laser Desorption/Ionization

An atmospheric pressure matrix assisted laser desorption ionization source (AP-MALDI, MassTech, Inc., Columbia, MD) was coupled to the QTrap Triple-Quadrupole mass spectrometer and used without alteration. The system provided direct analysis of inorganic species without matrix-assisted ionization, solvent, or other sample preparation. Briefly, the LDI system included a 355 nm wavelength Ng:Yag laser, pulsed at 150 Hz, with 150 $\mu\text{J pulse}^{-1}$ and 3 ns to 5 ns duration. A ± 3000 V potential was applied the sample substrate for all positive and negative mode experiments, respectively (Figure 1).

2.2.3 Support Instrumentation

Supplementary bulk quantification of extracted samples was completed using ion chromatography (IC) and inductively coupled plasma (ICP)-MS. A Dionex 5000-IC system (Thermo Scientific, Bannockburn, IL) with a CS-18 cation ion exchange column was utilized. The analysis included a 25 μL injection, 30 $^{\circ}\text{C}$ column temperature, 0.5 mL min^{-1} eluent flow

rate of 7 mM methanesulfonic acid buffer in ion chromatography grade water (Sigma-Aldrich), and a 35 °C detector compartment with an 11 mA suppression on the total conductivity detector. A calibration curve for potassium chlorate in the range of 0 ng μL^{-1} to 50 ng μL^{-1} was created and used to quantify triplicate injections of the extractions. Similarly, the extracted samples were also quantified using an iCAP-Q ICP-MS (Thermo Scientific, Bannockburn, IL). The samples were introduced into an argon plasma at 0.4 mL min^{-1} via nebulization. Again, a calibration curve ranging from 0 ng μL^{-1} to 50 ng μL^{-1} was created and used to quantify triplicate measurements of each extraction sample.

2.3 Evaluation of Uncertainty

The uncertainty in quantification of unknown samples from linear least squares calibration was evaluated in accordance with standard guidelines [41, 42]. Sources of measurement uncertainty were considered from the gravimetric preparation of standard solutions and the linear least squares calibration. The uncertainty in the calibration standard concentration included components from the solute purity, balance calibration, and fluctuations in room temperature. The purity of the compounds used here was given as $\geq 99.0\%$ by the manufacturer. Without additional information, a purity and uncertainty of $99.5 \pm 0.5\%$ was assumed, resulting in an expanded uncertainty ($k = 2$) of 1.0 %. The uncertainty in the tared weighing included the reproducibility (2 μg , AT21 comparator balance, Mettler Toledo), readability (1 μg), and the sensitivity/linearity of the balance calibration function ($\pm 8\ \mu\text{g}$). These uncertainties from the balance technical specifications were used to estimate the total expanded uncertainty ($k = 2$) as 0.33 %. Standard preparation was completed in an environmentally controlled laboratory with ambient temperature of $(23 \pm 1)^\circ\text{C}$. For the milliliter volumes considered here and assuming a coefficient of volume expansion for water of $2.1 \times 10^{-4}^\circ\text{C}^{-1}$, the expanded uncertainty ($k = 2$) in

the volume due to temperature was 0.04 %. These expanded uncertainties were combined in quadrature for a total uncertainty in the calibration curve standard concentration of 1.1 %.

The uncertainty in the quantification of samples was evaluated from a linear least squares calibration curve comprised of n unweighted data points (x_i, y_i) and p unknown sample measurements. Here x and y represented the standard concentration (c) and the measurement intensity (*e.g.*, signal intensity, I). The calibration curve was given by, $y = mx + b$, where m and b are the slope and intercept. The standard uncertainty in the unknown concentration due to variability in the response was determined by, $u(c_o, I) = S/m \sqrt{1/p + 1/n + (c_o - \bar{c})^2/S_{xx}}$, [41] where S is the root mean square error (determined by curve fitting with MATLAB, Version 2013a, The Mathworks Inc., Natick, MA) [43], c_o is the evaluated concentration of the unknown sample, $\bar{c}$ is the average concentration from the curve values, $S_{xx} = \sum (c_i - \bar{c})^2$, and c_i is the concentration of the i^{th} calibration point. The uncertainty in an unknown concentration due to variability in the reference calibration values, c_i , was approximated as, $u(c_o, x) = u(c_i)/n$ [41].

As demonstrated below, the uncertainty in the quantification of unknown samples due to variability in the system response outweighed the variability due to the reference standard concentrations.

3. Results and Discussion

3.1 Mass Spectral Characteristics of Explosive Oxidizers

Inorganic explosive oxidizers were analyzed by laser desorption/ionization mass spectrometry (LDI-MS) with in-source CID. Sample substrates were oriented orthogonal to the mass spectrometer inlet as displayed in Figure 1. The main oxidizers investigated here included PC, PPC, PN, AN, and CAN. Figure 2 demonstrates the representative spectra for 1 μ g PPC in

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4 positive and negative ion mode at high (+ 300 V) and low (- 100 V) in-source CID potential,
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6 respectively. The application of an elevated in-source CID potential led to acceleration of ion
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8 clusters and adducts, resulting in increased fragmentation. The increase in fragmentation of
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10 larger clusters and adducts enhanced the detection of elemental inorganic ions by 10-fold to
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12 1000-fold (depending on the compound) for LDI-MS.
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17 In positive mode at high in-source CID (Figure 2a), the mass spectrum for PPC shows
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19 elemental cations and isotopic distributions for potassium (m/z 39 K^+), chromium (m/z 52 Cr^+),
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21 iron (m/z 56 Fe^+), and a potassium chlorine cluster (m/z 113 K_2Cl^+). The isotopic distribution and
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23 tandem mass spectrometry (MS/MS) of the m/z 113 peak corroborated identification (Figure
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25 2a(inset)). The chromium and iron peaks were identified in all positive mode spectra and
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27 attributed to components of the metal substrate used for parametric experiments. In negative
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29 mode at lower in-source CID (Figure 2b), the mass spectrum for PPC displayed major
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31 polyatomic anion peaks and isotopic distributions for perchlorate (m/z 99 ClO_4^-) and a potassium
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33 perchlorate cluster (m/z 237 $K(ClO_4)_2^-$), which was confirmed with an MS/MS scan at 54 V
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35 (Figure 2b(inset)).
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42 The remaining inorganic oxidizers displayed similar mass spectra in positive and
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44 negative ion mode. Briefly, in high CID positive mode, PC and PN displayed cation peaks for
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46 potassium (m/z 39 K^+), chromium (m/z 52 Cr^+), and iron (m/z 56 Fe^+). The potassium chlorine
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48 cluster (m/z 113 K_2Cl^+) observed for PPC was also observed for PC. The molecular cation for
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50 ammonium fell outside the detectable m/z range of the present instrument and could not be
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52 observed. The negative ion mass spectra of PC at low in-source CID displayed the chlorate anion
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54 (m/z 83 ClO_3^-), and a potassium chlorate cluster (m/z 205 $K(ClO_3)_2^-$), which displayed the correct
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56 isotopic distributions (MS/MS in supporting information Figure S1a). Both nitrate (m/z 62 NO_3^-)
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4 and nitrite (m/z 46 NO_2^-) were observed for PN, AN, and CAN in negative mode. Similar to PC
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6 and PPC, a cluster of potassium and nitrate (m/z 163 $\text{K}(\text{NO}_3)_2^-$) was observed for PN and
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8 corroborated by MS/MS (Figure S1b).
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10 11 12 **3.2 In-Source CID Optimization** 13 14

15 Following an initial characterization of the main peaks observed for each inorganic
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17 oxidizer, an in-depth characterization of in-source CID was completed using
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19 residues/reconstituted particles from solution deposits. In-source CID was utilized to directly
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21 control the extent of cluster and adduct formation and fragmentation. In addition, the extent of
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23 molecular anion fragmentation could be directly controlled with in-source CID. As discussed in
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25 detail elsewhere [34, 44-46], unlike the specific m/z fragmentation of MS/MS, CID impartially
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27 induces acceleration of all ions and collisions with atmospheric gas molecules in the MS inlet
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29 region. Here, each oxidizer was interrogated while varying the extent of in-source CID through
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31 the instrument declustering potential. Potentials were increased from ± 25 V to ± 375 V in 25 V
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33 increments for positive and negative mode experiments, respectively, collecting a mass spectrum
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35 for 5 s at each interval.
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42 Figure 3 displays the MS signal (integrated peak area), normalized by the maximum
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44 signal, for the anions of each inorganic oxidizer as a function of increasing in-source CID
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46 potential. Data points and uncertainties represent the average peak area and standard deviations
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48 for 5 to 8 replicate samples. The signal response of these polyatomic inorganic anions differed
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50 from those previous found for organic explosives and elemental cations [34]. Previous work
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52 investigating organic explosives demonstrated a nearly monotonically decreasing response as a
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54 function of in-source CID potential. However, as seen in Figure 3, the molecular anions, derived
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56 from salt starting materials, displayed an initial increase in signal with in-source CID, a local
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4 maximum, followed by a decrease of varying degree. In addition to variability in the rate of
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6 decrease in signal beyond the maximum, the in-source CID potential for optimal signal intensity
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8 was dependent on the analyte. These phenomena were determined to be directly related to the
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10 ionic bond strength of the starting ionic material (*e.g.*, potassium chlorate), and the bond
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12 strength/molecular stability of the molecular anion (*e.g.*, chlorate). In the regime of increasing
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14 signal with increasing CID potential, the stronger the ionic bond, the lower the initial signal
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16 strength (*i.e.*, at - 25 V CID) and the higher the in-source CID potential at the maximum signal.
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18 Here, the MS response trends correlated with the energy necessary to break the ionic bonds and
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20 fragment salt-anion clusters (*e.g.* $\text{K}(\text{ClO}_4)_2^-$, Figure 2b). As demonstrated in Figure 3, the overall
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22 salt bond strength, via enthalpy of formation, increased from AN ($-365.6 \text{ kJ mol}^{-1}$), CAN
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24 (unknown combination of ammonium nitrate and calcium nitrate with enthalpies of formation of
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26 $-365.6 \text{ kJ mol}^{-1}$ and $-938.2 \text{ kJ mol}^{-1}$, respectively), PC ($-397.7 \text{ kJ mol}^{-1}$), PPC ($-432.8 \text{ kJ mol}^{-1}$),
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28 to PN ($-494.6 \text{ kJ mol}^{-1}$), resulting in optimal in-source CID potentials of -100 V, -125 V, -125 V,
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30 -150 V, and -275 V, respectively.
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39 Following the optimal extent of CID for breaking up the cation-anion ionic bond and salt-
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41 anion clusters, further increase in the energy and frequency of collisions resulted in
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43 fragmentation of the anion molecule, *e.g.*, ClO_3^- . The overall anion bond strength, again via
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45 enthalpy of formation, increased from chlorate ($-98.3 \text{ kJ mol}^{-1}$), to perchlorate ($-131.4 \text{ kJ mol}^{-1}$),
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47 to nitrate ($-206.6 \text{ kJ mol}^{-1}$). The direct visualization of these trends in Figure 3 was convoluted by
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49 a number of factors, specifically variability in the energy threshold for breaking the salt ionic
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51 bonds among compounds and the mixture of ammonium nitrate and calcium nitrate found in
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53 CAN. For example, when comparing the responses of PN and AN, at a mid-range in-source CID
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55 potential (*e.g.*, -200 V), a larger fraction of the imparted energy went into breaking of the
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4 potassium-nitrate bond relative to the ammonium-nitrate bond. More specifically, the majority of
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6 the available energy went into breaking the potassium-nitrate ionic bond, while only a fraction
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8 was needed to break the ammonium-nitrate ionic bond and the remaining available energy went
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10 into fragmenting the nitrate anion (Figure 3). The enthalpy of formation, and bond strength, of
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12 the PN salt was the highest considered here and resulted in a wide local maximum and minimal
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14 fragmentation of the nitrate anion.
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19 The anion fragmentation behavior was further investigated using tandem mass
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21 spectrometry (MS/MS) of AN, PC, and PPC. Product ion mass spectra for each anion resulted in
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23 expected fragments (Figure S2). Similar to scanning the declustering potential, the collision cell
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25 voltage was scanned from 25 V to 100 V in 5 V increments collecting a product ion mass
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27 spectrum for 5 s at each interval. Using the optimal in-source CID potential found above, the
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29 MS/MS spectra were taken at -100 V, -125 V, and -150 V CID potential for AN, PC, and PPC,
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31 respectively. Figure 4a displays the response for each anion as a function of collision cell
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33 voltage. The anions were fragmented, identifying transitions from nitrate into nitrite (m/z 46
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35 NO_2^-); chlorate into chlorite (m/z 67 ClO_2^-) and hypochlorite (m/z 51 ClO^-); and perchlorate into
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37 chlorate, chlorite, and hypochlorite (Figure 4 and S2).
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44 Similar to the results demonstrated for the molecular anions in Figure 3, Figure 5a
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46 displays the MS response of a few main clusters observed as a function of in-source CID. The
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48 clusters, $\text{K}(\text{ClO}_3)_2^-$, $\text{K}(\text{ClO}_4)_2^-$, and $\text{K}(\text{NO}_3)_2^-$, confirmed the results presented in Figure 3,
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50 revealing higher initial signals for the weaker salts and higher in-source CID potentials for
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52 maximum signal intensity. As observed in previous investigations [34], elemental ions
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54 demonstrated the opposite response, asymptotically increasing in signal with increasing in-
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56 source CID potential (Figure 5b-5d). Figure 5b displays the relative response of the potassium
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cation from PC, PPC, and PN. The elemental cations cannot be further fragmented and therefore did not demonstrate any reduction in signal above a local maximum for the range of CID potentials investigated here. However, an asymptotic approach to a maximum signal was observed. Figure 5c displays the response for the metal fuel zinc, the chloride anion from PPC, and calcium cation from CAN, all exhibiting the expected trends for elemental ions. Additional metal fuels such as aluminum and magnesium fell outside the m/z range optimized for this investigation and were not readily detected. In-source CID provides the critical fragmentation of clusters to enhance the detection of these inorganic explosives. The trace detection of explosive device signatures may also require detection of non-explosive components. For example, radiological dispersion devices incorporate obtainable industrial radionuclides used in medical radiotherapy, sterilization, or power generation, to be dispersed by a primary explosive. In-source CID was employed in Figure 5d to demonstrate the detection of stable isotope surrogates for cobalt (^{59}Co representing ^{60}Co) and strontium (^{88}Sr representing ^{90}Sr) in place of the radionuclide isotopes.

3.3 Inorganic Oxidizer Detection and Chemical Imaging

The framework developed above for optimization of in-source CID of both molecular and elemental inorganic components was leveraged for the detection of fuel-oxidizer mixtures using an LDI-MS instrument with in-source CID. The laser desorption ionization source was fitted with a CCD camera and on-screen display for manual interrogation of regions of interest (ROIs) and individual particles. Figure 6 displays an image and mass spectrum associated with the direct examination of a particle and residue area spiked on a latent fingerprint. For demonstration purposes, potassium perchlorate crystals were crushed and dry transferred onto a deposited latent fingerprint on a nickel chromium substrate. The ROIs identified in Figure 6a were analyzed

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4 using both automated meandering (serpentine) scans at 10 mm min^{-1} and direct manual
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6 interrogation of the particle (Figure 6b). Distinct peaks corresponding to chlorate (m/z 83),
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8 perchlorate (m/z 99), and the previously identified potassium perchlorate cluster (m/z 237
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10 $\text{K}(\text{ClO}_4)_2^-$) were observed. Given preexisting knowledge of the inorganic oxidizer, the optimal
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12 in-source CID potential (-150 V) was utilized for the detection of potassium perchlorate.
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15 However, for unknown samples, rapid scans through CID potentials within the transition from
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17 crystal fragmentation to anion fragmentation, demonstrated in Figure 3, would cover the optimal
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19 parameter value for a range of oxidizers. This mode of specific user defined interrogation may be
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21 applied to the detection of other explosive particles (organic: nitramines, nitroaromatics, nitrate
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23 esters, peroxides, etc.), radionuclide particles, and gunshot residues/particles from fingerprints
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25 and forensic tape pulls.
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32 In addition, for bulk detection and avenues toward quantification of specific analytes dry
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34 transferred onto fingerprints, the latent fingerprint containing potassium perchlorate
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36 particles/residues was extracted from the substrate surface in $200 \text{ }\mu\text{L}$ of water. The print extract
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38 was then deposited in $1 \text{ }\mu\text{L}$ aliquots and allowed to dry before direct analysis by LDI-MS. Figure
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40 6c displays the mass spectrum for a 45 s scan of the extracted aliquot deposit, clearly displaying
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42 the chlorate and perchlorate peaks previously identified. Additional peaks likely associated with
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44 the fingerprint material and other contaminants were also observed. The extraction process also
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46 provided sufficient dissolution of the potassium perchlorate crystals to significantly reduce the
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48 intensity of the cluster at m/z 237 ($\text{K}(\text{ClO}_4)_2^-$) and introduce a potassium-chlorate-perchlorate
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50 cluster at m/z 221 ($\text{K}(\text{ClO}_3)(\text{ClO}_4)^-$), previously not observed (Figure 6c).
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57 Next, we investigated the bulk quantification capabilities for the analysis of inorganic
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59 explosive containing residues using LDI-MS and in-source CID. For this analysis trace residues
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4 were collected on adhesive sheets during the synthesis of homemade potassium chlorate and
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6 icing sugar materials for a simulated fuel-oxidizer mixture device. The three samples, labeled A,
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8 B, and C, were extracted and calibration curves were prepared as described above. For LDI-MS,
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10 1 μL aliquots were deposited onto sample plates and the solvent allowed to evaporate under
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12 ambient conditions. The calibration curve consisted of samples in the range of 0 $\text{ng } \mu\text{L}^{-1}$ to 50 ng
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14 μL^{-1} . Each sample was interrogated by the laser for 15 s and mass spectral data was collected and
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16 summed. In-source CID potentials of +350 V and -125 V were used for the quantification and
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18 calibration curves of the elemental potassium cation and molecular chlorate anion. The
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20 calibration curves for potassium and chlorate were linear in the range of 0 $\text{ng } \mu\text{L}^{-1}$ to 25 $\text{ng } \mu\text{L}^{-1}$
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22 and 0 $\text{ng } \mu\text{L}^{-1}$ to 50 $\text{ng } \mu\text{L}^{-1}$, respectively (Figure S3). The calibration curves were utilized for
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24 quantification of extracted samples, as well as to approximate the limits of detection (LOD) for
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26 the LDI-MS system. The LOD was defined as the deposited mass generating an analyte-specific
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28 peak that resulted in a signal-to-noise ratio of 3:1. From potassium chlorate, the LODs measured
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30 for the potassium cation (Figure S3a) and chlorate anion (Figures S3b) were both at the
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32 nanogram level. Similarly, nitrate based oxidizers, AN and CAN, also demonstrated nanogram
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34 level LODs, for detection of the nitrate anion.
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44 The three unknown samples (A-C) were then each measured in triplicate and the results
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46 listed in Table 1. The standard uncertainty from the linear least squares calibration was evaluated
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48 as described in the Methods section. The potassium signal for sample A was measured above the
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50 linear region of the calibration curve and excluded. For confirmation, the potassium cation from
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52 the 2 mL extracted solutions was also analyzed using ICP-MS and IC. As shown in Table 1, the
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54 LDI-MS quantification between the potassium cation and chlorate anion were comparable to
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56 each other, as well as consistent with the potassium cation measurements across the alternative
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4 techniques. However, due to the nature of the measurement, the uncertainty in the LDI-MS
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6 system response was greater than the other techniques. The ICP-MS and IC measurements
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8 directly analyzed the relatively homogenous extracted solutions. Replicate measurements by
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10 these methods were in essence taken on the same sample. On the contrary, LDI-MS relied on the
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12 deposition of solution phase aliquots and analysis of the solid phase remaining after solution
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14 evaporation. This significant difference in the manner of sample preparation can result in non-
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16 uniform surface concentrations and thicknesses, which in turn affect the actual amount of
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18 material interrogated. These aspects may have led to the large uncertainties in the calibration
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20 curve and bulk quantification measurements by LDI-MS. This method was clearly inadequate for
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22 quantification for masses near the limit of detection (*e.g.*, sample C). In spite of this potential
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24 shortcoming, the direct analysis of particles has the potential to provide additional information,
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26 specifically, molecular speciation of individual particles, beyond the bulk extraction and analysis
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28 of analyte distributions. Similarly, mass spectrometry imaging (MSI) of the spatial distribution of
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30 particles and chemical distributions of analytes on a surface or within a complex matrix might
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32 provide complementary forensic information.
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41 Similar to the method above, the LDI-MS system was utilized for the chemical imaging
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43 of organic and molecular inorganic compounds from a latent fingerprint. Again, particles of
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45 potassium perchlorate or calcium ammonium nitrate were dry transferred onto latent fingerprints
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47 on a nickel/chromium substrate and imaged without sample preparation, pretreatment, or the use
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49 of matrix. Prints were imaged in $100\ \mu\text{m} \times 100\ \mu\text{m}$ pixels across individual $5\ \text{mm} \times 5\ \text{mm}$
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51 regions of interest at constant $12.5\ \text{mm min}^{-1}$ velocity. Figure 7 demonstrates the chemical
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53 images of an endogenous lotion component, behentrimonium $m/z\ 368\ \text{M}^+$, perchlorate $m/z\ 99$
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55 ClO_4^- , and the potassium perchlorate cluster $m/z\ 237\ \text{K}(\text{ClO}_4)_2^-$. The lotion component,
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4 behentrimonium, was imaged in positive mode and detectable at a relatively wide range of in-
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6 source CID potentials (Figure 7a). The potassium component of the PPC particles was
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8 unsuccessfully resolved in positive mode at high in-source CID due to interference with
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10 potassium from the latent fingerprint as well as the underlying substrate surface. The elemental
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12 potassium cation distribution was dominated by the machining marks left on the sample substrate
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14 surface (image not shown). The perchlorate (Figure 7b) and potassium perchlorate cluster
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16 (Figure 7c) distributions were clearly resolved in negative mode MS at low in-source CID (-150
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18 V) and demonstrated colocalization (Figure 7d), further substantiating the identification of the
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20 m/z 237 cluster.
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27 Figure 7e and 7f display a surface map of the lotion component and the corresponding
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29 intensity line scan across a series of print ridges, respectively. The technique demonstrated
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31 spatial resolution on the order of 100's μm , sufficient for an overall characterization of the
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33 analyte distributions, yet insufficient for differentiating much smaller micron size particles or
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35 tertiary ridge detail. Alternative high resolution laser desorption [47] and time-of-flight
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37 secondary ion mass spectrometry (ToF-SIMS) [48] systems can provide the sub-micrometer
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39 spatial resolution necessary for particles sizing and pore imaging.
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45 The chemical distribution imaging of another oxidizer, calcium ammonium nitrate,
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47 successfully identified the calcium cation (m/z 40 Ca^+), the nitrate anion (m/z 62 NO_3^-), and a
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49 calcium nitrate cluster at m/z 226 $\text{Ca}(\text{NO}_3)_3^-$ (Figure S4). The ROI was interrogated twice, first at
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51 high in-source CID (+300 V) in positive mode for the chemical distribution of the elemental
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53 calcium cation, and then at low in-source CID (-100 V) in negative mode for the distributions of
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55 nitrate and the calcium nitrate cluster. The nitrate and calcium nitrate cluster collocated
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57 demonstrating the particle/residue distribution (Figure S4b). However, the calcium cation and
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4 nitrate chemical images demonstrated the same general distributions, but were not as precisely
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6 collocated (Figure S4a). In some instances the calcium cation image displayed a much smaller
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8 size distribution of individual particles as compared to the nitrate distributions. These artifacts
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10 may be due to a number of artifacts, including non-uniform distributions of calcium nitrate and
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12 ammonium nitrate, slight variability in the two consecutive scans, variability in the initial
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14 particle shape and the post-scan particle shape (the first scan interrogated and ablated the apex of
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16 a particle, while the second scan experienced a wider mid-section of the particle), variability in
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18 the particle/residue distribution at different sample depths, or nitrate dissolution into the eccrine
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20 component of the fingerprint. The LDI-MS system enabled direct control over the laser power
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22 and pulse frequency, providing a potential means for investigating the applicability of depth
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24 profiling with this technique.
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35 **4. Conclusions**

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38 The analysis and detection of explosive device signatures from a transient collection of
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40 homemade and improvised explosives and devices remains a clear area of interest. Inorganic
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42 compounds including fuel-oxidizer and self-initiating mixtures, azides, and radionuclides, play a
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44 critical role in an assembly of HMEs and IED components. Here, we presented the coupling of
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46 in-source collision induced dissociation (CID) with atmospheric pressure laser
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48 desorption/ionization mass spectrometry (LDI-MS) for the detection, bulk quantification, and
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50 chemical imaging of fuel-oxidizer mixture signatures. In-source CID enhanced detection of
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52 elemental inorganic ions by 10-fold to 1000-fold through the fragmentation of larger adducts and
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54 clusters, as well as through the reduction in organic chemical noise. Similarly, in-source CID
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56 was utilized to identify the optimal CID potential, providing 10-fold to 100-fold increase in
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4 signal, for the detection of oxidizer polyatomic anion components, specifically, nitrates,
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6 chlorates, and perchlorates. This optimization was identified at the transition between
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8 energetically breaking the ionic salt bonds and fragmenting the molecular anion. The optimized
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10 detection of elemental and molecular inorganic ions enabled the detection of inorganic explosive
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12 components at nanogram levels. The developed framework was leveraged for their detection
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14 from a complex matrix, the bulk quantification of realistic samples collected during explosive
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16 synthesis, and chemical imaging of oxidizer particles from latent fingerprints. The use of LDI-
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18 MS for quantification demonstrated inherently large uncertainty in the system response. Future
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20 work will explore the use of inkjet printing for the controlled deposition of calibration standards
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22 and the incorporation of an internal standard. Precision drop-on-demand inkjet printing has the
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24 potential to provide micron-scale uniform sample deposits for linear least squares calibration and
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26 quantification. In addition, the LDI-MS system enabled direct control over the laser power and
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28 pulse frequency, providing a potential means for investigating high density inorganic particles
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30 for environmental monitoring, radionuclide isotopic ratio analysis, and biological tissue imaging.
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32 Future work will also aim to explore these opportunities.
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References

- [1] Lang, G.-h.L. and K.M. Boyle, The Analysis of Black Powder Substitutes Containing Ascorbic Acid by Ion Chromatography/Mass Spectrometry, *J. Forensic Sci.* **54** (2009) 1315-1322.
- [2] Dicinoski, G.W., R.A. Shellie, and P.R. Haddad, Forensic Identification of Inorganic Explosives by Ion Chromatography, *Anal. Lett.* **39** (2006) 639-657.
- [3] Hutchinson, J.P., C.J. Evenhuis, C. Johns, et al., Identification of Inorganic Improvised Explosive Devices by Analysis of Postblast Residues Using Portable Capillary Electrophoresis Instrumentation and Indirect Photometric Detection with a Light-Emitting Diode, *Anal.Chem.* **79** (2007) 7005-7013.
- [4] Corr, J.J. and J.F. Anacleto, Analysis of Inorganic Species by Capillary Electrophoresis–Mass Spectrometry and Ion Exchange Chromatography–Mass Spectrometry Using an Ion Spray Source, *Anal.Chem.* **68** (1996) 2155-2163.
- [5] Bottegal, M., L. Lang, M. Miller, et al., Analysis of ascorbic acid based black powder substitutes by high-performance liquid chromatography/electrospray ionization quadrupole time-of-flight mass spectrometry, *Rapid Commun. Mass Spectrom.* **24** (2010) 1377-1386.
- [6] Ewing, R.G., D.A. Atkinson, G.A. Eiceman, et al., A critical review of ion mobility spectrometry for the detection of explosives and explosive related compounds, *Talanta* **54** (2001) 515-529.
- [7] Kolakowski, B.M. and Z. Mester, Review of applications of high-field asymmetric waveform ion mobility spectrometry (FAIMS) and differential mobility spectrometry (DMS), *Analyst* **132** (2007) 842-864.

- [8] Najarro, M., M.E. Davila Morris, M.E. Staymates, et al., Optimized thermal desorption for improved sensitivity in trace explosives detection by ion mobility spectrometry, *Analyst* **137** (2012) 2614-2622.
- [9] Verkouteren, J.R., J. Lawrence, G.A. Klouda, et al., Performance metrics based on signal intensity for ion mobility spectrometry - based explosive trace detectors using inkjet printed materials, *Analyst* **139** (2014) 5488-5498.
- [10] Ehlert, S., A. Walte, and R. Zimmermann, Ambient Pressure Laser Desorption and Laser-Induced Acoustic Desorption Ion Mobility Spectrometry Detection of Explosives, *Anal.Chem.* **85** (2013) 11047-11053.
- [11] Liang, X., Q. Zhou, W. Wang, et al., Sensitive Detection of Black Powder by a Stand-Alone Ion Mobility Spectrometer with an Embedded Titration Region, *Anal.Chem.* **85** (2013) 4849-4852.
- [12] Khayamian, T., M. Tabrizchi, and M.T. Jafari, Analysis of 2,4,6-trinitrotoluene, pentaerythritol tetranitrate and cyclo-1,3,5-trimethylene-2,4,6-trinitramine using negative corona discharge ion mobility spectrometry, *Talanta* **59** (2003) 327-333.
- [13] Tabrizchi, M. and V. Ilbeigi, Detection of explosives by positive corona discharge ion mobility spectrometry, *J. Hazard. Mater.* **176** (2010) 692-696.
- [14] Justes, D.R., N. Talaty, I. Cotte-Rodriguez, et al., Detection of explosives on skin using ambient ionization mass spectrometry, *Chem. Commun.* (2007) 2142-2144.
- [15] Szakal, C. and T.M. Brewer, Analysis and Mechanisms of Cyclotrimethylenetrinitramine Ion Formation in Desorption Electrospray Ionization, *Anal. Chem.* **81** (2009) 5257-5266.
- [16] Takats, Z., I. Cotte-Rodriguez, N. Talaty, et al., Direct, trace level detection of explosives on ambient surfaces by desorption electrospray ionization mass spectrometry, *Chem. Commun.* (2005) 1950-1952.
- [17] Cotte-Rodríguez, I., Z. Takáts, N. Talaty, et al., Desorption Electrospray Ionization of Explosives on Surfaces: □ Sensitivity and Selectivity Enhancement by Reactive Desorption Electrospray Ionization, *Anal. Chem.* **77** (2005) 6755-6764.
- [18] Nilles, J.M., T.R. Connell, S.T. Stokes, et al., Explosives Detection Using Direct Analysis in Real Time (DART) Mass Spectrometry, *Propell., Explos., Pyrot.* **35** (2010) 446-451.

- [19] Sisco, E., J. Dake, and C. Bridge, Screening for trace explosives by AccuTOF™-DART®: An in-depth validation study, *Forensic Sci. Int.* **232** (2013) 160-168.
- [20] Forbes, T.P., T.M. Brewer, and G. Gillen, Desorption electro-flow focusing ionization of explosives and narcotics for ambient pressure mass spectrometry, *Analyst* **138** (2013) 5665-5673.
- [21] Zhang, Y., X. Ma, S. Zhang, et al., Direct detection of explosives on solid surfaces by low temperature plasma desorption mass spectrometry, *Analyst* **134** (2009) 176-181.
- [22] Garcia-Reyes, J.F., J.D. Harper, G.A. Salazar, et al., Detection of Explosives and Related Compounds by Low-Temperature Plasma Ambient Ionization Mass Spectrometry, *Anal. Chem.* **83** (2010) 1084-1092.
- [23] Takáts, Z., J.M. Wiseman, B. Gologan, et al., Mass Spectrometry Sampling Under Ambient Conditions with Desorption Electrospray Ionization, *Science* **306** (2004) 471-473.
- [24] Cody, R.B., J.A. Laramée, and H.D. Durst, Versatile New Ion Source for the Analysis of Materials in Open Air under Ambient Conditions, *Anal. Chem.* **77** (2005) 2297-2302.
- [25] Harris, G.A., A.S. Galhena, and F.M. Fernández, Ambient Sampling/Ionization Mass Spectrometry: Applications and Current Trends, *Anal. Chem.* **83** (2011) 4508-4538.
- [26] Ifa, D.R., C. Wu, Z. Ouyang, et al., Desorption electrospray ionization and other ambient ionization methods: current progress and preview, *Analyst* **135** (2010) 669-681.
- [27] *Counterterrorist Detection Techniques of Explosives*, J. Yinon, Editor Elsevier, B.V., Amsterdam, 2007.
- [28] *Aspects of Explosive Detection*, M. Marshall and J.C. Oxley, Editors, Elsevier B. V., Amsterdam, 2009.
- [29] Dalby, O., D. Butler, and J.W. Birkett, Analysis of Gunshot Residue and Associated Materials—A Review, *J. Forensic Sci.* **55** (2010) 924-943.
- [30] Mäkinen, M., M. Nousiainen, and M. Sillanpää, Ion spectrometric detection technologies for ultra-traces of explosives: A review, *Mass Spectrom. Rev.* **30** (2011) 940-973.
- [31] Cotte-Rodríguez, I., H. Hernández-Soto, H. Chen, et al., In Situ Trace Detection of Peroxide Explosives by Desorption Electrospray Ionization and Desorption Atmospheric Pressure Chemical Ionization, *Anal. Chem.* **80** (2008) 1512-1519.

- [32] Cotte-Rodriguez, I., H. Chen, and R.G. Cooks, Rapid trace detection of triacetone triperoxide (TATP) by complexation reactions during desorption electrospray ionization, *Chem. Commun.* (2006) 953-955.
- [33] Parajuli, S. and W. Miao, Sensitive Determination of Triacetone Triperoxide Explosives Using Electrogenerated Chemiluminescence, *Anal. Chem.* **85** (2013) 8008-8015.
- [34] Forbes, T.P. and E. Sisco, Mass Spectrometry Detection and Imaging of Inorganic and Organic Explosive Device Signatures using Desorption Electro-Flow Focusing Ionization, *Anal. Chem.* **86** (2014) 7788-7797.
- [35] Evans-Nguyen, K.M., A. Quinto, T. Hargraves, et al., Transmission Mode Desorption Electrospray Ionization (TM-DESI) for Simultaneous Analysis of Potential Inorganic and Organic Components of Radiological Dispersion Devices (RDDs), *Anal. Chem.* **85** (2013) 11826-11834.
- [36] Flanagan, P.M., J.J. Brady, E.J. Judge, et al., Determination of Inorganic Improvised Explosive Device Signatures Using Laser Electrospray Mass Spectrometry Detection with Offline Classification, *Anal. Chem.* **83** (2011) 7115-7122.
- [37] Pavlov, J. and A.B. Attygalle, Direct Detection of Inorganic Nitrate Salts by Ambient Pressure Helium-Plasma Ionization Mass Spectrometry, *Anal. Chem.* **85** (2012) 278-282.
- [38] Forbes, T.P., Rapid detection and isotopic measurement of discrete inorganic samples using acoustically actuated droplet ejection and extractive electrospray ionization mass spectrometry, *Rapid Commun. Mass Spectrom.* **29** (2015) 19-28.
- [39] Forbes, T.P. and E. Sisco, Chemical Imaging of Artificial Fingerprints by Desorption Electro-Flow Focusing Ionization Mass Spectrometry, *Analyst* **139** (2014) 2982-2985.
- [40] Robichaud, G., K. Garrard, J. Barry, et al., MSiReader: An Open-Source Interface to View and Analyze High Resolving Power MS Imaging Files on Matlab Platform, *J. Am. Soc. Mass Spectrom.* **24** (2013) 718-721.
- [41] Ellison, S.L.R., M. Rosslein, and A. Williams, *Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement*. Second ed. 2000.
- [42] Taylor, B.N. and C.E. Kuyatt, NIST Technical Note 1297, Guidelines for evaluating and expressing the uncertainty of NIST measurement results, NIST Technical Note 1297, Guidelines for evaluating and expressing the uncertainty of NIST measurement results <http://www.nist.gov/pml/pubs/tn1297/> (1994).

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2
3
4 [43] *MATLAB*. 2013, The MathWorks Inc.: Natick, MA.
5
6 [44] Blades, A.T., P. Jayaweera, M.G. Ikononou, et al., Studies of alkaline earth and
7 transition metal M^{++} gas phase ion chemistry, *J. Chem. Phys.* **92** (1990) 5900-5906.
8
9 [45] Jayaweera, P., A.T. Blades, M.G. Ikononou, et al., Production and study in the gas phase
10 of multiply charged solvated or coordinated metal ions, *J. Am. Chem. Soc.* **112** (1990)
11 2452-2454.
12
13 [46] Watson, J.T. and O.D. Sparkman, *Introduction to Mass Spectrometry*. 2007, West
14 Sussex, John Wiley & Sons, Ltd.
15
16 [47] Elsner, C. and B. Abel, Ultrafast High-Resolution Mass Spectrometric Finger Pore
17 Imaging in Latent Finger Prints, *Sci. Rep.* **4** (2014) 1-6.
18
19 [48] Bailey, M.J., M. Ismail, S. Bleay, et al., Enhanced imaging of developed fingerprints
20 using mass spectrometry imaging, *Analyst* **138** (2013) 6246-6250.
21
22
23
24
25
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Figure Captions

Figure 1. Schematic representation of the laser desorption/ionization (LDI) mass spectrometry imaging setup, including in-source collision induced dissociation (CID).

Figure 2. Representative LDI mass spectra of 1 μg potassium perchlorate sampled for 30 s in (a) positive and (b) negative mode, at high (+ 300 V) and low (- 100 V) in-source CID, respectively. Insets: corresponding MS/MS product ion spectra of the m/z 113, K_2Cl^+ , and m/z 237, $\text{K}(\text{ClO}_4)_2^-$, clusters at ± 54 V collision cell voltage in positive and negative mode MS.

Figure 3. Normalized signal abundance as a function of in-source CID (declustering) potential magnitude for inorganic molecular anions from 1 μg explosive oxidizers: $\blacklozenge$ NO_3^- from AN, $\blacktriangle$ NO_3^- from CAN, $\blacklozenge$ ClO_3^- from PC, $\bullet$ ClO_4^- from PPC, $\blacksquare$ NO_3^- from PN. Data points and uncertainty expressed as the average peak area and standard deviations for 5 to 8 successive replicate samples, respectively.

Figure 4. Signal intensity, *i.e.*, integrated peak area, as a function of collision cell voltage for inorganic molecular anions in negative mode. (a) Response of anions originating from PPC: $\bullet$ m/z 99 ClO_4^- , PC: $\blacklozenge$ m/z 83 ClO_3^- , and AN: $\blacklozenge$ NO_3^- . Signal intensity of relevant anions in (b)–(d) also include fragments for nitrite: $\blacktriangle$ m/z 46 NO_2^- , chlorite: $\blacktriangle$ m/z 67 ClO_2^- and hypochlorite: $\blacksquare$ m/z 51 ClO^- . Data points and uncertainty expressed as the average peak area and standard deviations for 5 successive replicate samples, respectively.

Figure 5. Normalized signal abundance as a function of in-source CID (declustering) potential magnitude for (a) inorganic clusters in negative mode and (b) – (d) elemental cations in positive mode from 1 μg explosive oxidizers, metal fuels, and stable isotope radionuclide surrogates. (a) Negative mode inorganic clusters from PC: $\blacklozenge$ m/z 205 $\text{K}(\text{ClO}_3)_2^-$, PPC: $\bullet$ m/z 237 $\text{K}(\text{ClO}_4)_2^-$,

PN: m/z 163 $\text{K}(\text{NO}_3)_2^-$. Positive mode (b) potassium cations (m/z 39 K^+) from PPC, PC, and PN; (c) metal fuel zinc (m/z 65 Zn^+) and elemental components of PPC (m/z 35 Cl^-) and CAN (m/z 40 Ca^+); and (d) stable isotope radionuclide surrogates cobalt (m/z 59 Co^+) and strontium (m/z 88 Sr^+). Data points and uncertainty expressed as the average peak area and standard deviations for 5 to 8 successive replicate samples, respectively.

Figure 6. (a) Optical images of potassium perchlorate particles and residues on a latent fingerprint. (b) Representative LDI-MS mass spectra for the 2 min manual interrogation of the identified particle and adjacent residue from user defined ROIs (i) and (ii). (c) LDI-MS mass spectrum for the 45 s scan of a 1 μL sample from the full print liquid extraction. The base peak absolute intensity is noted in the upper right hand corner of each panel.

Figure 7. LDI-MSI of endogenous organic and polyatomic inorganic ions at low in-source CID: (a) endogenous lotion component – behentrimonium m/z 368, (b) perchlorate m/z 99 ClO_4^- , (c) potassium perchlorate cluster m/z 237 $\text{K}(\text{ClO}_4)_2^-$, and (d) the colocalization map of the lotion (blue) and potassium perchlorate particles/residues (represented by perchlorate ion distribution, red). (e) and (f) display a surface map of the lotion component and the corresponding intensity line scan across a series of print ridges, respectively.

Table Caption

Table 1. Mass of potassium chlorate detected from samples A-C. Calculated masses based on measurements of the potassium cation and chlorate anion using LDI-MS, ICP-MS, and IC. Standard uncertainties in the quantification of unknowns due to variability in the system response from linear least squares calibration were evaluated as described in the Methods section ($k = 1$).

Figures

Figure 1. Schematic representation of the laser desorption/ionization (LDI) mass spectrometry imaging setup, including in-source collision induced dissociation (CID).

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Figure 5. Normalized signal abundance as a function of in-source CID (declustering) potential magnitude for (a) inorganic clusters in negative mode and (b) – (d) elemental cations in positive mode from 1 μg explosive oxidizers, metal fuels, and stable isotope radionuclide surrogates. (a) Negative mode inorganic clusters from PC: $\diamond$ m/z 205 $\text{K}(\text{ClO}_3)_2^-$, PPC: $\bullet$ m/z 237 $\text{K}(\text{ClO}_4)_2^-$, PN: $\blacksquare$ m/z 163 $\text{K}(\text{NO}_3)_2^-$. Positive mode (b) potassium cations (m/z 39 K^+) from PPC, PC, and PN; (c) metal fuel zinc ($\blacklozenge$ m/z 65 Zn^+) and elemental components of PPC ($\bullet$ m/z 35 Cl^-) and CAN ($\blacktriangle$ m/z 40 Ca^+); and (d) stable isotope radionuclide surrogates cobalt ($\blacklozenge$ m/z 59 Co^+) and strontium ($\blacktriangle$ m/z 88 Sr^+). Data points and uncertainty expressed as the average peak area and standard deviations for 5 to 8 successive replicate samples, respectively.

Figure 6. (a) Optical images of potassium perchlorate particles and residues on a latent fingerprint. (b) Representative LDI-MS mass spectra for the 2 min manual interrogation of the identified particle and adjacent residue from user defined ROIs (i) and (ii). (c) LDI-MS mass spectrum for the 45 s scan of a 1 μL sample from the full print liquid extraction. The base peak absolute intensity is noted in the upper right hand corner of each panel.

Figure 7. LDI-MSI of endogenous organic and polyatomic inorganic ions at low in-source CID:

(a) endogenous lotion component – behentrimonium m/z 368, (b) perchlorate m/z 99 ClO_4^- , (c) potassium perchlorate cluster m/z 237 $\text{K}(\text{ClO}_4)_2^-$, and (d) the colocalization map of the lotion (blue) and potassium perchlorate particles/residues (represented by perchlorate ion distribution, red). (e) and (f) display a surface map of the lotion component and the corresponding intensity line scan across a series of print ridges, respectively.

Tables

Table 1. Mass of potassium chlorate detected from samples A-C. Calculated masses based on measurements of the potassium cation and chlorate anion using LDI-MS, ICP-MS, and IC.

Standard uncertainties in the quantification of unknowns due to variability in the system response from linear least squares calibration were evaluated as described in the Methods section ($k = 1$).

Technique	Sample A		Sample B		Sample C	
	K^+ (μg)	ClO_3^- (μg)	K^+ (μg)	ClO_3^- (μg)	K^+ (μg)	ClO_3^- (μg)
LDI-MS	-	34.5 ± 6.9	9.0 ± 2.9	8.1 ± 6.8	2.4 ± 2.6	1.7 ± 6.9
ICP-MS	36.5 ± 0.5		8.5 ± 0.5		2.1 ± 0.5	
IC	36.3 ± 0.4		9.7 ± 0.4		2.0 ± 0.4	