

Trace Detection and Chemical Analysis of Homemade Fuel-Oxidizer Mixture Explosives: Emerging Challenges and Perspectives

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Highlights

- Homemade fuel-oxidizer explosives present key challenges for field detection.
- Non-volatile refractory oxidizers exhibit poor thermal desorption efficiencies.
- Fuel-oxidizer mixture and environmental background can interfere with sensing.
- Analytical instrumentation and sensors are evolving to address these challenges.
- Advances focus on chemical conversion, liquid dissolution, and thermal desorption.

Abstract

The chemical analysis of homemade explosives (HMEs) and improvised explosive devices (IEDs) remains challenging for fieldable analytical instrumentation and sensors. Complex explosive fuel-oxidizer mixtures, black and smokeless powders, flash powders, and pyrotechnics often include an array of potential organic and inorganic components that present unique interference and matrix effect difficulties. The widely varying physicochemical properties of these components as well as external environmental interferents and background challenge many sampling and sensing modalities. This review provides perspective on these emerging challenges, critically discusses developments in sampling, sensors, and instrumentation, and showcases advancements for the trace detection of inorganic-based explosives.

1. Introduction & Scope of the Review

The trace detection, chemical analysis, and accurate identification of explosives remains critical not only for screening in the security sector by transportation authorities, customs and border protection, and law enforcement, but also for fieldable testing by forensic or criminal investigators and counterterrorism efforts. The vital needs to combat explosive-based terrorist attacks and provide sensitive and accurate material or device attribution have driven innovative and seminal advancements in analytical instrumentation,[1-3] novel sensor development,[4, 5] and fundamental energetic material characterization.[6, 7] Over the years, substantial research has advanced high-throughput screening and investigative analysis of energetic materials, most notably of typical military-grade nitrated organic high explosives. These secondary explosives commonly include nitroaromatics (*e.g.*, 2,4,6-trinitrotoluene, TNT), nitrate esters (*e.g.*, pentaerythritol tetranitrate, PETN), and nitramines (*e.g.*, 1,3,5-trinitro-1,3,5-triazinane, RDX). As the threat landscape has evolved, the use of homemade explosives (HMEs) and improvised explosive devices (IEDs) derived from more readily available materials has surged.[8] These range from unstable high-order primary explosives, including peroxides (*e.g.*, hexamethylenetriperoxide diamine, HMTD, and triacetone triperoxide, TATP), azides (*e.g.*, lead azide), and fulminates (*e.g.*, mercury fulminate), to stable low-order tertiary explosives or fuel-oxidizer mixtures (*e.g.*, ammonium nitrate-fuel oil, ANFO), propellants (*e.g.*, black and smokeless powders), and pyrotechnics (*e.g.*, flash powders). The recent 2019 Annual List of Explosive Materials published by the U.S. Bureau of Alcohol, Tobacco, Firearms, and Explosives includes over 240 explosive compounds and mixtures.[9]

The considerable variation in physicochemical properties of these compounds and mixtures presents challenges for chemical analysis and identification. These differences and difficulties are

clearly evident by the stark contrast in properties between typical organic fuels (*e.g.*, sugar, petroleum jelly, nitromethane) and inorganic oxidizers (*e.g.*, nitrate or perchlorate) in a range of fuel-oxidizer and self-initiating mixtures. Similarly, many low-order explosives require a secondary explosive primer or intermediate booster to initiate detonation, again presenting distinct differences in organic and inorganic components and their properties such as vapor pressure, solubility, state (solid particle, residue, liquid, or emulsion), particle size and morphology, and molecular stability. The necessity to address the key analytical challenges presented by these classes of explosive mixtures is only intensified by readily accessible and prevalent precursors. In addition, pyrotechnics, inorganic powders, propellants, and related mixtures consistently top the list of explosive device main charges used in the United States, as published in the annual Explosive Incident Report by the United States Bomb Data Center.[10] Though a plethora of analytical techniques have aided in various explosive detection, identification, and investigative attribution analyses, further challenges arise from the operational concepts for screening and fieldable environments.

This review focuses on the key and often unique challenges that trace detection of inorganic fuel-oxidizer explosives and related mixtures pose as well as critical discussion and perspectives on recent advances in the field. We provide a brief introduction to trace explosives detection concepts, including expansion into operational concepts for related applications targeting inorganic oxidizers/anions in screening or field deployable arenas. These include illicit pyrotechnics and fireworks interdiction, onsite forensic and criminal investigations, and environmental monitoring. This is followed by discussion of key measurement challenges, the nature of the threat, and difficulties arising from the chemical properties of inorganic oxidizers and interferences from fuels, other components, and environmental background. Finally, we discuss

notable avenues to address these challenges for improved detection, summarizing important developments from the literature that provide unique benefits or interesting results and addressing future prospects and directions.

2. Operational Concepts

2.1. General Concepts for Trace Explosive Detection

Accurate identification of synthesis precursors, explosive and device chemical signatures, and post-blast byproducts from residual contamination lies at the foundation of the operational concepts for trace explosives detection. In this review, we use “trace” to refer to both traditional trace samples (*i.e.*, samples unable to be seen or easily weighed – typically nanograms and below) and small bulk samples (*i.e.*, an intermediate level that can be seen but not easily weighed – milligram to microgram levels). This combination allows us to include technologies and instrumentation (*e.g.*, spectroscopy) that are currently applied to small bulk analysis but may have the potential sensitivity for trace detection with continued development.

Figure 1 provides a general illustration of the operational concepts typical of trace explosives detection. Residual contamination resulting from synthesis, handling, carrying, or general contact with an explosive or explosive device often resides on the exterior of target surfaces (*e.g.*, clothing, luggage, packages, vehicles, people, hands, etc.). The trace chemical residues found on surfaces are frequently individual particles on the order of micrometers in diameter embedded in latent fingerprints, vapor condensation, or lingering aerosol deposition.[11, 12] For applications related to checkpoint and onsite screening or field deployable analysis, portable instrumentation with favorable size, weight, and power (SWaP), low cost, and ease of use are preferred. In general this includes analytical techniques such as portable or handheld spectroscopy (*e.g.*, Raman or Fourier

transform infrared [FTIR],[13] spectrometry (*e.g.*, ion mobility spectrometry [IMS] or mass spectrometry [MS]),[14, 15] and colorimetric sensors.[16] Several of these techniques employ swipe sampling from target surfaces in order to maximize collection area and threat detection probability. Here, particulate material is collected from surfaces by physically swiping with a wipe, swab, or trap material (*e.g.*, Nomex, muslin, acetate paper, or polytetrafluoroethylene-coated fiberglass weave). The physically collected samples are then introduced to the analytical instrumentation through a thermal desorption process (Figure 1). The resultant aerosol/vapor mixture either directly interacts with sensing elements (*e.g.*, fluorescence quenching) or enters an ionization region prior to analysis (*e.g.*, IMS). Typically, signals from the select analytical technique or sensor are compared against a target library using a specified alarm algorithm and threshold for automated interpretation.

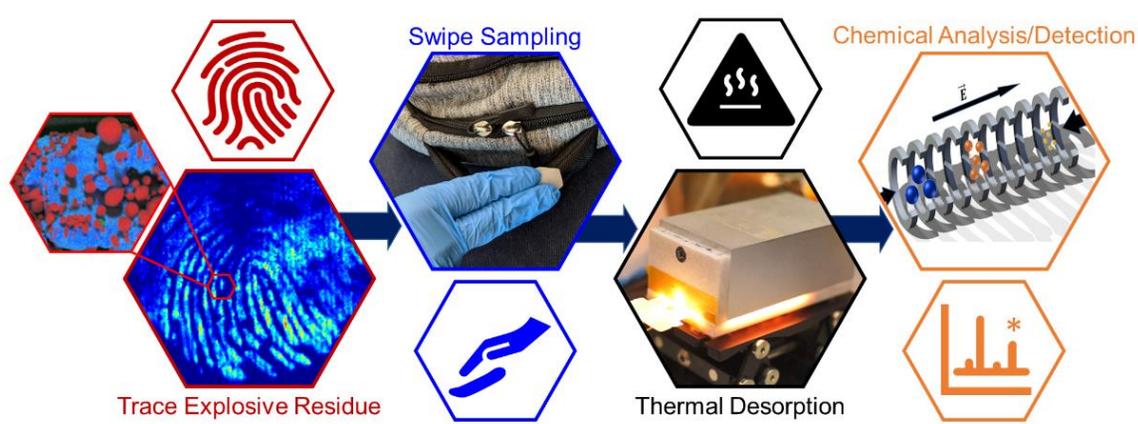


Fig. 1. Illustration of the key concepts for one example (*i.e.*, thermal desorption-IMS) of trace explosives detection. From left to right, a trace residue (both threat and background clutter particles) is collected through swipe sampling. This collection is thermally desorbed prior to chemical analysis and algorithm interpretation.

As detailed in the introduction, the USBDC’s annual Explosives Incident Report consistently finds inorganic-based low explosive propellants, tertiary explosive mixtures, and pyrotechnics among the most frequently used energetic components for IEDs in the United States. Although

inorganic-based low explosive propellants, tertiary explosive mixtures, and pyrotechnics contain multiple components, trace explosives detection applications related to the security sector commonly target the inorganic oxidizers of these homemade explosives. The few typical inorganic oxidizers provide a higher level of specificity relative to the wide array of potential fuels. These oxidizers are most commonly nitrates, chlorate, and perchlorates, with permanganates, nitrites, and hypochlorites used less frequently. Alternatively, fuel sources can be anything delivering a source of electrons, including hydrocarbons – petroleum jelly, kerosene, fuel oil, waxes, or solvents; carbohydrates – sugars (icing sugar or gummy bears), starches (flour), or cellulose; powdered metals – aluminum, magnesium, or zinc; non-metals – sulfur, carbon, or phosphorus; and even energetic fuels – nitromethane or dinitrotoluene. The large number and variety of potential fuels makes their differentiation from background difficult. The same inorganic oxidizers and associated anions play a major role in illicit pyrotechnics interdiction, post-blast forensic investigations, and onsite environmental monitoring and contamination studies.

2.2. Illicit Pyrotechnics Screening

Numerous federal jurisdictions throughout the world regulate production, transportation, international trade, and sale of fireworks and related materials.[17, 18] These regulations vary widely from country to country, but in general target the illicit use and movement of commercial pyrotechnics and the counterfeit manufacture of pyrotechnics. Postal and inspection agencies often rely on human intelligence or other evidence for targeted intervention, visual examination for suspicious appearance, random checks, or more traditional bulk screening methods (*e.g.*, X-ray detection). The use of chemical detection platforms for illicit pyrotechnics interdiction mainly

relies on the signatures of the inorganic oxidizers (*e.g.*, perchlorate from potassium perchlorate-aluminum flash powder), but also target the fuels when feasible (*e.g.*, sulfur in black powders).[19]

2.3. Onsite Forensic Analysis and Investigation Support

Interest in fieldable instrumentation for the accurate identification of inorganic explosives and related materials is not limited to screening applications. Forensic and crime scene investigations often require rapid chemical analysis to identify unknown materials in clandestine laboratories, as well as efficiently and effectively direct ongoing efforts.[20] This onsite analysis bypasses the time-consuming delays imposed by sending evidence to a laboratory for chemical analysis, enabling immediate action on gathered information and intelligence. Similarly, first responders and investigators may initially confront unknown chemicals that are potentially hazardous or unstable and sensitive to insult (*e.g.*, heat, shock, electrostatic discharge, or chemical decomposition). Understanding the nature of encountered materials, through rapid identification, is vital to the safety of response teams. Chemical information from fieldable analytical techniques can prove critical to steering forensic investigations, maintaining first responders and civilian safety, and guiding the handling and removal of hazardous materials.

2.4. Fieldable Environmental Monitoring

Further, *in situ* detection and identification of these inorganic species is vital to environmental monitoring and remediation efforts for areas of land and water polluted by firework displays.[21] Environmental contamination by nitrate, chlorate, and perchlorate can impact both ecological and human health. Elevated levels of these compounds have been associated with various health hazards resulting from leaching into agricultural products, the greater food chain, and ground and

surface water. While these salts are found naturally in mineral deposits, they also have anthropogenic origins, including fertilizer (nitrate); disinfection by-products, dye manufacturing, or herbicides (chlorate/perchlorate); and oxidizers for solid propellants, fireworks, or air-bag initiators (perchlorate). Though monitoring of these environmental contaminants often entails sample extraction and transportation to a laboratory for analysis, on-site inspections also play a role, requiring rapid field instrumentation similar to the above applications.[22]

Here, we focus on the underlying commonality throughout these applications, specifically, the fieldable trace detection of inorganic-based fuel-oxidizer explosives, propellants, and pyrotechnics. Next, we detail the key measurement challenges for inorganic oxidizer detection from such complex mixtures pose, highlighting the difficulties that arise for common analytical techniques and sensors, ambient ionization platforms, and sampling by traditional thermal desorption approaches.

3. Key Measurement Challenges

The detection of explosive fuel-oxidizer mixtures presents a number of key measurement challenges revolving around the physical and chemical characteristics of the target species (*i.e.*, inorganic oxidizers), as well as interference, suppression, and other matrix effects from both the other target mixture components (*e.g.*, fuels or fillers) or environmental compounds. These challenges are summarized in Table 1 and discussed in detail here.

Table 1. Key measurement challenges and impact on the detection of target oxidizers from explosive fuel-oxidizer mixtures, and potential solutions or avenues for improvement.

Key Measurement Challenge	Impact on Oxidizer Detection	Potential Solutions
Trace particulate threat material	Low probability for collection (and detection) Low area relative to target surface area	Large area sampling methods (<i>e.g.</i> , swipe sampling) Rapid sampling and collection methods

Low vapor pressure refractory salts	Minimal vapor at room temperature for direct vapor detection Elevated temperatures needed for efficient thermal desorption	Reagent-based chemical conversion to more volatile conjugate acid Dissolution in liquid High temperature thermal desorption
Ionic cluster and adduct formation	Wide ion distribution yielding numerous alarm channels Reduced sensitivity by spreading signal across adducts/clusters	In-source collision induced dissociation manipulating ion distribution Dopant addition for preferential ionization pathways Judicious choice of separation buffer
Interference from fuels and additives	Dark fuels suppress colorimetric detection Ignition from laser excitation of spectroscopic techniques Complex mixtures yield matrix effects (<i>e.g.</i> , signal suppression)	Dissolution and physical separation Preferential ionization schemes Judicious choice of separation buffer Orthogonal detection capabilities
Interference from environmental background	False detection from environmentally occurring anions Signal suppression and matrix effects from complex background Background fluorescence	High selectivity techniques Advanced alarm algorithms / adjusted thresholds

3.1. Nature of the Threat

While the full intact molecule is commonly targeted for organic nitrated explosives, most often only the inorganic molecular anions of the oxidizer are targeted for the overarching class of propellants, pyrotechnics, and explosive powders. Detection of the oxidizers is highly dependent on the nature of the fuel-oxidizer mixture. Generally, the performance of these explosives, pyrotechnics, and propellants is a function of the intimate nature of the mixture, defined by the proximity of reactants and the particle surface areas, as well as the oxygen balance and thermodynamics. The reactant proximity and particle surface areas are a function of the mixture's physical properties, specifically, particle size and mixture homogeneity. Contrastingly, the oxygen balance and thermodynamics are a function of the mixture's chemical properties. For example, this may be as simple as a binary mixture of a powdered fuel (*e.g.*, aluminum) and a powdered oxidizer (*e.g.*, ammonium nitrate), or a complex mixture such as emulsion blasting explosives, which may also include components such as mineral oil, sorbitan monooleate, paraffin, polyisobutylene succinic anhydride, or other polymeric emulsifiers.

Typical fuel-oxidizer mixtures consist of particles of a refractory inorganic oxidizer such as ammonium nitrate (NH_4NO_3), potassium nitrate (KNO_3), potassium chlorate (KClO_3) or potassium perchlorate (KClO_4). These oxidizers are physically mixed with a fuel such as hydrocarbons (*e.g.*, petroleum jelly), carbohydrates (*e.g.*, icing sugar), non-metals (*e.g.*, sulfur), and powdered metals (*e.g.*, aluminum). As introduced above, the vast range of potential fuels and their potential prevalence among background species limits any utility to their detection. Though not typically necessary for explosive detection, the associated fuels may interfere with sensing modalities. Similarly, repurposed fireworks often include flash powders composed of potassium perchlorate and aluminum powder. Firework oxidizers also incorporate alternative cations to achieve desired color profiles, for example, strontium for a red hue or barium for a green hue. Primitive black powder propellants contain a simple mixture of potassium nitrate, sulfur and carbon. However, a wide array black powder substitutes of various compositions have been developed to include other inorganic and organic oxidizers and fuels.

The simple synthesis of these homemade explosives (*i.e.*, mixing of two or more components) and availability of precursors encourages their use for illicit purposes. The homemade nature of these explosives alone makes characterizing the expected physical properties *a priori* challenging. For this reason, there is little published data regarding trace residues from homemade fuel-oxidizer mixtures. Yet, in the absence of reference data on homemade mixtures, characterization of commercially available pyrotechnics, propellants, and other crude fuel-oxidizer explosives may provide insight into potential properties, morphologies, and relative abundances.

3.2. Trace Particulate Threat

The total mass of these materials contaminating target surfaces as trace explosive residues may be extremely small. Surface coverage of such residues may also be very low relative to overall area (*e.g.*, surface area of a package of vehicle). Swipe sampling offers a rapid means of collection and concentration from large surface areas. Optimal sampling of fuel-oxidizer mixture residues by swipe sampling relies on best practices developed for sampling of conventional explosives, including targeting of high touch areas, using appropriate force during collection, and collecting threat particles on the most relevant location on the wipe to ensure efficient thermal desorption.

3.3. Low Vapor Pressure Refractory Salts

The thermal desorption and vaporization of wipe-collected target species is foundational to sample introduction for a wide range of deployed technologies for trace contraband (*e.g.*, explosives and narcotics) detection. This often includes traditional analytical techniques, such as IMS or MS, but also extends into more novel sensors, such as amplified fluorescence polymer sensors. This process conventionally utilizes constant temperature thermal desorbers optimized for the widest detection of target species possible. Maintaining efficient thermal desorption of compounds with vastly different chemical properties, specifically those related to the desorption process, is a significant challenge. This challenge is simply demonstrated by the differences in, for example, volatile peroxide-based explosives (*e.g.*, TATP) and non-volatile fuel-oxidizer explosives (*e.g.*, fuel oil-potassium chlorate). Many of the refractory inorganic oxidizers found in these mixtures, most notably chlorate and perchlorate salts, exhibit low vapor pressures, estimated to be below 1×10^{-15} Pa.[23] In order to efficiently and effectively vaporize the oxidizer for subsequent detection and identification, elevated thermal desorption temperatures must be incorporated. However, significantly raising steady-state thermal desorption temperatures leads to

difficulties associated with the thermal decomposition of more labile organic targets. Elevated temperatures can also effectively flash desorb analytes, yielding a very brief signal duration. The temporal extent of analyte may be detrimental to analytical techniques with duty cycle limitations.

3.4. Ionic Cluster and Adduct Formation

The chemical nature of target oxidizers (*i.e.*, ionic salts) presents another unique challenge for analytical techniques based on transport of ions in electric or magnetic fields, for example, IMS and MS. These techniques use various mechanisms to ionize analyte (and background clutter) species prior to measurement. Under these conditions, free cations and anions have a propensity to form larger clusters and adducts with neutral organic species, including organic explosives and other target compounds. Such extensive ion distributions not only create an overwhelming number of “alarm channels” that must be monitored but the ion distributions also reduce sensitivity by spreading signal across these adducts and clusters.

3.5. Interference from Fuels, Additives, and Environmental Background

In addition to these difficulties, analytical instruments and sensors must overcome confounding matrix effects both from other components of the mixture itself and the environment. Homemade fuel-oxidizer explosives might be based on a simple binary mixture or a more complex propellant with an assortment of fuels and oxidizers. For example, the propellant Triple Seven black powder substitute contains organic and inorganic fuels and oxidizers, including potassium nitrate, potassium perchlorate, sodium benzoate, charcoal, dicyandiamide, dextrin, and nitrobenzoic acid. These supplementary mixture components may act as background “clutter” and interfere with the detection scheme, resulting in a false negative. For example, colorimetric tests targeting oxidizers

from propellants, pyrotechnics, or fuel-oxidizer mixtures must overcome interferences created by visibly dark fuels (*e.g.*, charcoal or aluminum). Complex mixtures may also present difficulties with competitive ionization and signal suppression for ion-based techniques (*e.g.*, IMS). Confounding interferences may also originate from the sampling environment, which can include compounds collected with the target sample (*e.g.*, fingerprint laden compounds) or environmental background levels (*e.g.*, inherent nitrate levels in soil or nitrates on cardboard packages). This environmental clutter may result in either false negatives by interfering with target detection or false positives by occurring at a target alarm channel or background levels above an alarm threshold level.

In the next section, we discuss recent avenues being considered for addressing these key measurement challenges. These have been organized into chemical and physical means, focusing predominately on the common wipe-based sample introduction procedures. We also touch on stand-off spectroscopic developments.

4. Avenues for improved detection

A number of recent developments have sought to address the key measurement challenges faced by the trace detection of inorganic homemade explosives (Table 1). These analytical methods can most easily be categorized by the initial chemical or physical process employed for the detection scheme, for example, chemical conversion (Section 4.1), physical dissolution (Section 4.2), and physical desorption (Section 4.3) (Figure 2). Spectroscopic techniques (*e.g.*, Raman or FTIR) are also briefly discussed for direct sampling (Section 4.4). Though extensive laboratory-based analytical instrumentation has commonly been used for the analysis of inorganic

species and explosives, we focus here on critical advances targeting fieldable applications as described above.

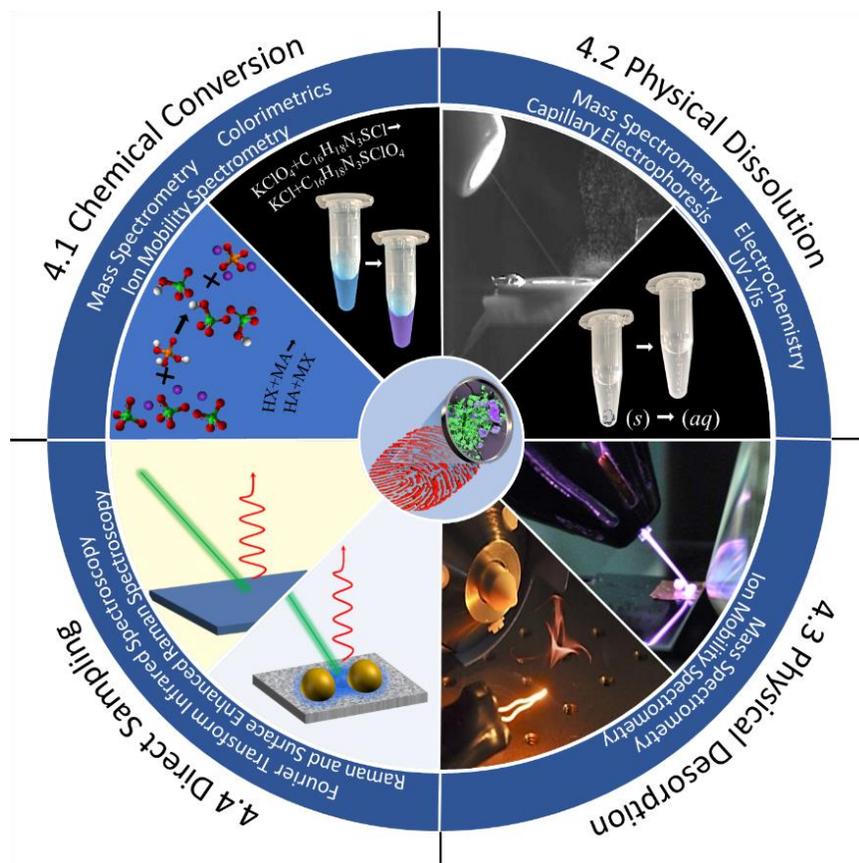


Fig. 2. Schematic representation of the main avenues for improved inorganic fuel-oxidizer mixture detection based the sample processing step(s) between collection and chemical analysis. The four quadrants represent the main categories discussed in Sections 4.1 – 4.4. Center: trace residue; inner ring: representative examples of conversion methods in each category; outer ring: example analytical techniques applicable to each category listed circumferentially.

4.1 Chemical Conversion

Chemical conversion avenues seek to chemically alter the oxidizers or an interacting sensing compound either as a sample processing step or the detection scheme itself. One of the simplest and most field portable chemical conversion techniques encompasses the wide array of colorimetric sensors. Colorimetric sensing has been utilized as a rapid detection method for explosives and narcotics based on a resultant chromophore upon addition of a chemical conversion

reagent. Typical inorganic oxidizer sensing reagents consist of methylene blue, aniline sulfate, and a modified Griess test for perchlorate, chlorate, and nitrate detection, respectively. Colorimetric sensors remain advantageous in several screening and detection scenarios due to the low cost, portability, speed, and simplicity in use and interpretation, owing to the value of these sensors for both field and laboratory use. In the simplest implementation, colorimetric sensing is employed as several chemical reagents contained in dropper bottles, ampules, or aerosol sprays. The reagents are used individually, with each indicative of a different target analyte to delineate an explosive compound or class of compounds. Reviews by Giannoukos, *et al.* and Kangas *et al.* describe colorimetric sensing platforms in more detail with a focus on portable security operations and explosives detection.[24, 25]

Colorimetric techniques relying on static chemical conversion (*i.e.*, reagent is deposited directly on sampled material) face interference in color-change observation from fuels such as charcoal or aluminum. These fuels and similar components significantly darken the sample-reagent mixture making visualization difficult. More recently, strides have been made toward multiplexed colorimetric sensors utilizing filter or chromatography paper for fluidic control. Dynamic chemical conversion in these techniques allow for separation and filtration of color-suppressing fuels. These sensors also increase user safety by limiting chemical exposure to reagents for sample identification. Peters *et al.* developed a microfluidic paper-based device that contained five colorimetric sensing locations for simultaneous analysis of inorganic oxidizers including nitrate, nitrite, chlorate and perchlorate, in addition to ammonium within five minutes.[16] This research group developed a subsequent paper-based microfluidic device for the simultaneous detection of common metals found in primer residues and pyrotechnics including lead, barium, antimony, iron, aluminum, zinc, and magnesium.[26]

The user's subjective visual interpretation of color change has long been a key challenge for colorimetric sensors. However, the ubiquity of portable imaging and photo processing tools (*e.g.*, smartphones, tablets, and cameras), has enabled objective image analysis for interpreting results and reducing errors related to user color interpretation or environmental influences.[27, 28] Since inception, digital imaging has been more frequently discussed in the format of a smartphone with corresponding application software.[29, 30] Recent advanced commercial products have coupled swipe sampling with reagent cards and integrated color analysis.[31] In addition, Askim *et al.*, has also demonstrated colorimetric arrays with gas-phase sampling using an internal micropump.[32] The sensor contained forty chemoresponsive dyes applied to sixteen relevant explosive compounds.

Further, novel sensors evolving from traditional colorimetric sensors have been developed. Wang *et al.* recently introduced an artificial olfactory system based on colorimetric hydrogel sensing for the detection and identification of airborne explosive vapors or microparticles.[33] The colorimetric hydrogel array allowed for discrimination between hypochlorite, chlorate, perchlorate, urea, and nitrate based salts. With response times of less than 1 second and 10 cycle reusability of the base hydrogel network, these sensors have encapsulated the solution reagents, an attractive advancement in field portable sensing technology. In addition, by leveraging existing and well characterized colorimetry chemistries, expected levels of environmental interferences can be presumed.

One promising new chemical conversion-based approach for analysis of inorganic oxidizers utilizes thermal desorption in conjunction with the addition of acidic reagents to the sampling wipe. These reagents enhance analyte vapor concentration by producing a more volatile conjugate acid of the salt anion.[34, 35] Original implementation of this approach was demonstrated by Peng *et*

al. for IMS analysis of inorganic oxidizer particles of potassium perchlorate, potassium chlorate, and potassium nitrate on polytetrafluoroethylene-coated fiberglass weave sampling wipes (Figure 3).[34] The experimental procedure involved spraying 3% phosphoric acid (H_3PO_4) solutions directly onto the sample containing wipe prior to thermal desorption. The acidification provided as much as a factor of 3000 increase in characteristic signal response for the inorganic oxidizers. Importantly, the signal enhancement via acidification was also noted in mixtures of the inorganic oxidizers with sugar, a commonly encountered fuel, suggesting this approach would be relevant to real world oxidizer-fuel mixtures. A potential limitation with practical application of this method is that many field portable IMS systems are not compatible with liquid reagents. Similarly, there is potential for corrosion of the common ^{63}Ni ion source and internal components of the ion mobility spectrometer. Kelley *et al.* concurrently explored the acidification approach using detection by MS, demonstrating signal enhancement factors as high as 10^6 for detection of potassium perchlorate.[35] Additional refinements emphasized practical application using unmodified IMS systems configured for field deployment. This includes eliminating the need for liquid acidification reagents by using thermally activated solid state acidification/hydration chemistries incorporated directly onto the collection wipe before sampling. These chemistries included, for example, the use of sodium bisulfate or Nafion with or without addition of an in situ hydration source.[35] This approach is attractive as it involves chemical modification of the sampling wipe and can potentially be implemented using existing trace detection instruments without significant modification.

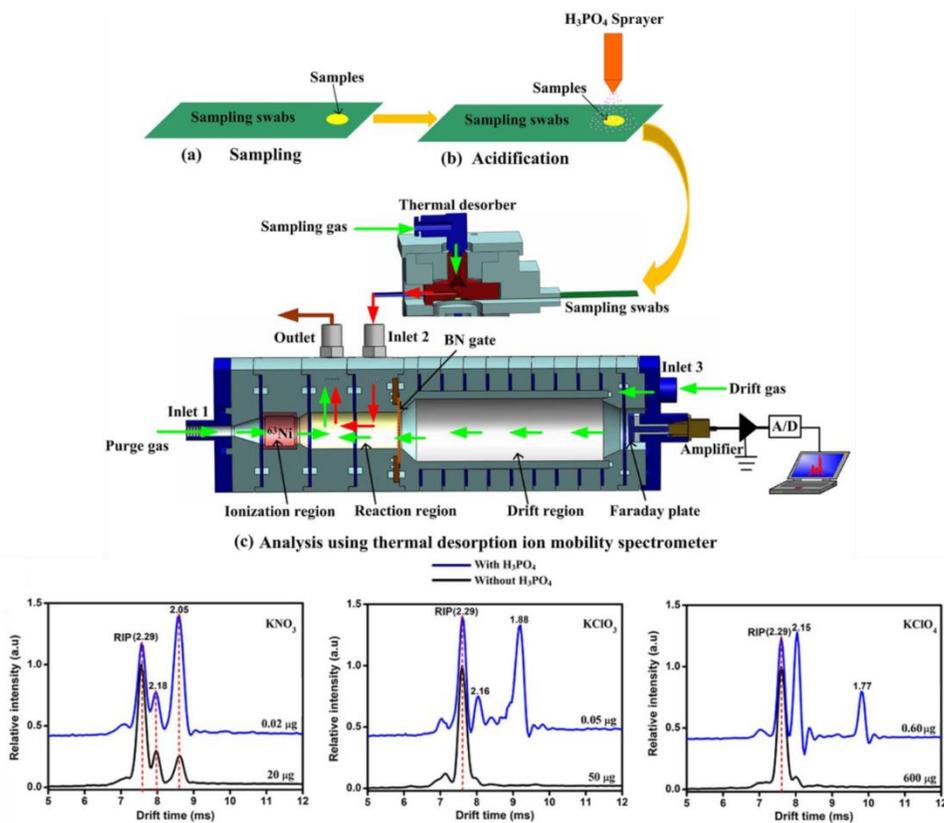


Fig. 3. Schematic representation of acidic reagent chemical conversion for thermal desorption ion mobility spectrometry of inorganic oxidizers. Representative ion mobility spectra of inorganic oxidizers with and without chemical conversion. Reproduced from reference [34] with permission from Springer Nature under a Creative Commons Attribution-NonCommercial-NoDerivs 4.0 International License (CC BY-NC-ND 4.0).

In addition to chemical conversion of target oxidizers to optically visible complexes or more volatile conjugate acids, various chemosensors incorporate conjugated polymers, photonic crystal films, or metal-organic frameworks.[36] These sensors include amplified fluorescence polymer and other chemiluminescence-based techniques.[4, 5, 37, 38] Binding by target analytes results in a detectable change in the sensing element. Though some systems report limited applicability to inorganic explosives (*e.g.*, only sulfur, urea nitrate, and ammonium nitrate),[37, 38] these sensors have almost exclusively focused on organic explosives. Alternatively, Li *et al.* developed a TiO₂ nanosheet-based gas sensor array targeting 11 explosives, including potassium nitrate, potassium

chlorate, potassium permanganate, sulfur, ammonium nitrate, and urea.[39] The chemiresistive sensor array demonstrated differentiation of the target organic and inorganic fuels and oxidizers with response times on the order of tens of seconds. A small set of interferences was investigated, however, the relatively low selectivity of the sensor has the potential for burdensome levels of false positive detections.

4.2 Physical Dissolution

The chemical conversion methods discussed in Section 4.1 sought to alter the target species into a more useful compound (based on the sampling or sensing processes) or a sensing complex. As we've introduced, the low vapor pressure for many common oxidizers presents difficulties for sample introduction methods based on traditional thermal desorption. In this section, we consider analytical techniques that incorporate a physical dissolution of the non-volatile refractory salt oxidizers into a relevant liquid.

Capillary electrophoresis (CE) is an analytical separation technique that incorporates sample dissolution for inorganic identification. CE utilizes an applied high potential and electrolyte buffer to separate charged inorganic ions within a capillary based on their electrophoretic mobilities. This technique was first applied to inorganic explosive residue in 1992 by Hargadon and McCord for the successful separation and detection of eight oxidizer anions present in four different pipe bomb samples.[40] Traditionally a laboratory technique, Kappes and Hauser introduced a portable CE instrument for the analysis of inorganic cations and anions in river water.[41] Subsequent portable instrumentation developments by Hutchinson *et al.* focused on the detection of both inorganic oxidizer cations and anions in post-blast residues utilizing differing electrolytes and applying both indirect photometric detection using an LED, and later transitioned to a capacitively coupled

conductivity detection (C⁴D) format.[42, 43] C⁴D is advantageous for inorganic ion detection with portability and ease of use, however, simultaneous detection of anions and cations presents a challenge due to the opposing charges and similar electrophoretic mobilities of cation species. A number of studies have demonstrated detection of a range of inorganic anions and cations in separation times from a minute to a few minutes.[44-46]

The majority of CE developments for inorganic detection have required some level of manual sample preparation for introduction of a liquid-based sample. While straight forward for applications such as environmental wastewater analysis, sample preparation can be cumbersome for screening scenarios. More recently, a commercial CE instrument, based on work by Blanco *et al.*, has been developed for targeted detection of nitrate, chlorate and perchlorate.[44, 47] This platform couples wipe-based sample introduction and automated extraction with a portable CE.[47] In 2020, Bezemer *et al.* applied this technology towards forensic analysis of confiscated packages from a postal facility for the detection of regulated fireworks material.[19] Similar to matrix effects exhibited for spectrometric techniques, excessive components or environmental clutter can alter buffer concentrations enough to shift migration times and inhibit alarm algorithms. Such challenges must always be considered for direct sample insertion platforms.

Related analytical techniques incorporating sample dissolution include ion selective electrodes (ISE),[48-50] electroanalytical sensors,[51] and spectrophotometry. These sensors include a wide array of materials and configurations, including use of single walled carbon nanotubes (SWCNTs), ionic liquids, or conductive polymer membranes. Platforms using electrochemical sensing and ion selective electrodes provide high specificity detection and have been deployed for inorganic anion detection from wastewater and even perchlorate from soil on Mars.[22, 48, 49] Recent work by Hassan *et al.*, developed a solid-contact ISE based on SWCNTs and an indium-porphyrin

ionophore for the detection of perchlorate from fireworks and propellants (Figure 4).[50] The ISE sensor provided an under 10 second response time and selective detection of perchlorate with no interference from common pyrotechnic fuels (*e.g.*, charcoal, sulfur, aluminum) or binders (*e.g.*, dextrin and lactose). However, relatively extensive sample preparation was completed prior to sample introduction, which hinders the applicability of this class of sensor for fieldable or screening scenarios. Applications in environmental monitoring could benefit from the continuous sensing capabilities directly in a body of water.

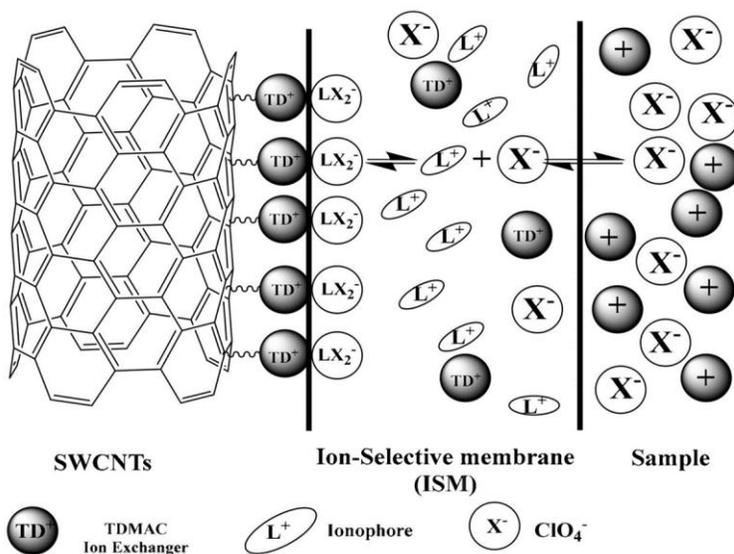


Fig. 4. Schematic representation of transduction for solid-contact ISE based on SWCNT and an indium-porphyrin ionophore. Reproduced from reference [50] with permission from MDPI (Multidisciplinary Digital Publishing Institute) under a Creative Commons Attribution 4.0 International License (CC BY 4.0).

Shriver-Lake *et al.* introduced an electroanalytical sensor for chlorate detection that incorporated a filter paper substrate impregnated with catalyst and screen-printed carbon electrodes.[51] Though the sensor was developed for incorporation into autonomous unmanned aerial vehicles or drones, the paper-based substrate provided a simple solution for direct wipe-based trace detection. The paper substrate also demonstrated concurrent filtration of soil samples

and an eight-month shelf life. A number of electrochemical and spectrophotometric sensors have also been developed for the field measurement of environmental nitrate and explosive oxidizer detection.[22, 52] Vakilian and Massah developed a portable platform that couples enzyme-based biosensing with electrochemical and ultraviolet-visible-near-infrared spectroscopic detection.[53] The device was designed for nitrate detection from samples including water, plant extract, and saliva. While interesting and potentially useful for targeted field detection, the limited detectable compounds (*e.g.*, only nitrate) hinder such platforms from wider use.

Finally, the evolution of ambient ionization platforms for MS, and specifically solid-liquid extraction techniques, has provided a sample introduction scheme based on both solvent dissolution and desorption. This class of techniques employs a charged solvent stream, which impinges a target surface and forms a thin film. Surface-laden analytes within the region of this small pool of solvent are dissolved, extracted, and carried to the mass spectrometer inlet in secondary droplets. Traditionally, these techniques follow classical electrospray ionization (ESI) mechanisms. Sokol *et al.* successfully demonstrated the sampling and detection of nitrate, chlorate, perchlorate, and sulphate oxidizers off a range of surfaces using one of the first ambient ionization platforms introduced and based on ESI – desorption electrospray ionization (DESI).[54] Judicious choice of DESI spray solvent provided direct dissolution of trace oxidizer levels from these surfaces. Similar techniques, including easy ambient sonic spray ionization (EASI) and desorption electro-flow focusing ionization (DEFFI), have also sought to take advantage of key ambient ionization advantages, including a lack of necessary sample preparation, rapid analysis, and direct sampling from surfaces *in situ*. Hernandez *et al.* used EASI-MS for the forensic identification of tertiary explosives off debris and currency from an ATM (automatic teller machine) theft explosion.[55]

These electrospray ionization-based techniques have a propensity for generating clusters and adducts from targeted oxidizers with solvent molecules and other organic species from the sample. A number of ambient and atmospheric pressure ionization MS studies have used in-source collision induced dissociation (CID) to manipulate the ion distributions of inorganic anions.[56, 57] In-source CID ensues through the acceleration of ions within the differentially pumped region of mass spectrometers. This acceleration leads to an increase in the frequency and energy of collisions with remaining neutral gas molecules, fragmenting larger clusters and adducts. Forbes and Sisco manipulated in-source CID to optimize for organic or inorganic explosives and demonstrated detection of both fuels and oxidizers from lifted fingerprints and wipe-collected samples.[58] Though the solid-liquid extraction ambient ionization techniques described here were implemented on laboratory-based mass spectrometers, similar sources have been coupled with portable instruments for forensic analysis in the field.[59, 60]

4.3 Physical Desorption

In this section, we expand from the dissolution methods of Section 4.2 into physical desorption techniques that integrate either elevated temperatures for direct thermal desorption, high energy sputtering, or physical ablation. High power plasmas or laser-based techniques have sufficient energy to desorb and ionize the inorganic explosives of interest. For example, Evans-Nguyen *et al.* developed a microwave plasma ambient ionization source that was capable of directly interrogating elemental fuels as well as organic nitrated explosives for mass spectrometric analysis (ion trap).[61] However, high power plasmas are typically destructive to a large number of other compounds of interest (*e.g.*, decomposition and fragmentation) or underlying substrate materials, and require significant power and gas consumption. Direct laser ablation has also been

demonstrated by Reiss *et al.* in the form of a handheld sampling probe with transfer line coupled to a mass spectrometer.[62] This atmospheric pressure laser desorption was capable of directly interrogating surfaces of interest in a semi-remote manner and detecting organic explosives and ammonium nitrate, however, potassium perchlorate and potassium chlorate were not detected in the range investigated ($< 2000 \mu\text{g}$).[62]

A number of platforms incorporating high temperature thermal desorption have demonstrated utility for vaporizing refractory inorganic oxidizers for downstream analysis. These approaches have focused on two underlying configurations: one employing direct resistive heating of a metal mesh or wire collector, and the other coupling traditional wipe-based samples with infrared heating. Metal meshes have been used both as a wipe material for sampling directly from surfaces and as a preconcentrator, collecting aerosols or liberated particles. Resistively heating the mesh generates a rapid and discrete transient temperature profile. The heating ramp enables collected species to thermally desorb at their optimal temperatures – volatile components at relatively lower temperatures and non-volatile components at elevated temperatures. Early implementations of this approach were demonstrated with traditional organic military explosives, coupled to a range of detection schemes, including proton transfer reaction MS and IMS. Recent embodiments have used rapid heating of metal wire collectors for high temperature desorption of refractory chlorate and perchlorate salts and mass spectrometric analysis.[23, 63] Ewing *et al.* used a resistively heated wire for desorption of a range of inorganic chlorate, perchlorate, and nitrate salts for analysis using atmospheric flow tube (AFT) MS.[23] With a dielectric barrier discharge ionization source, AFT-MS yielded an array of ions ranging from bare salt anions to larger clusters and adducts with free nitrate. Forbes *et al.* coupled a similar nichrome wire with direct analysis in real time (DART) MS for the detection of comparable species.[64] Temperatures up to $750 \text{ }^\circ\text{C}$ were generated, yielding

regimes of thermal desorption and thermal decomposition. Analogous to the DEFFI-MS work discussed above, in-source CID was also used to manipulate the large(r) ion distributions exhibited by inorganic salts. Though yet to be demonstrated on portable instrumentation, there is a clear path for employing elevated temperature heating of wire or mesh substrates for field applications. However, as a preconcentrator, these meshes would still depend on a method to liberate particles of interest; and as a wipe material, these meshes may cause damage to sensitive items (*e.g.*, laptops or hands).

In a related high temperature platform, Forbes *et al.* incorporated infrared heating and traditional wipe sampling to thermally desorb organic and inorganic explosives (Figure 5).[64-66] Given the wide variability in infrared absorption of targeted compounds, this thermal desorber used infrared energy to rapidly heat a secondary energy storage component in direct contact with an inserted wipe. The infrared thermal desorption (IRTD) temperature profiles desorbed volatile components (*e.g.*, sulfur or ascorbic acid) early in the profile and nonvolatile components (*e.g.*, potassium perchlorate or potassium nitrate) late(r) in the profile. This inherent ramp enables temporal separation of complex mixtures, a useful capability for forensic analysis. The IRTD platform has been coupled with both atmospheric pressure chemical ionization (APCI) and DART ionization schemes for either MS or IMS analysis. In addition, the incorporation of commercially available wipes and rapid heating/cooling processes support implementation for high-throughput screening applications. However, care must be taken with appropriate temperatures for instrument transfer components downstream of thermal desorption. The refractory inorganic salts have the potential to re-condense on surfaces prior to analysis causing carryover complications.

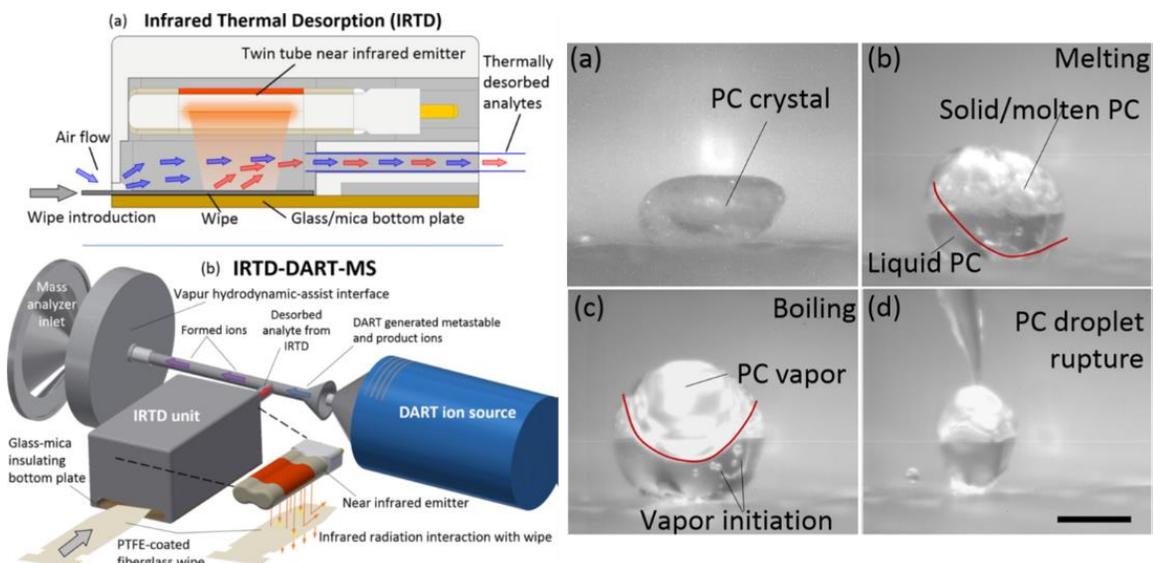


Fig. 5. Schematic illustration of the infrared heating process and overall IRTD-DART-MS system. Visualization of IRTD heating of potassium chlorate particle (scale bar: 250 μm). PC: potassium chlorate. Reprinted with permission from reference [64]. Copyright 2018 American Chemical Society.

4.4 Spectroscopy of Solids

Finally, we discuss surface sampling avenues by spectroscopic techniques. FTIR and Raman spectroscopy have been widely used for characterization of both organic and inorganic explosive compounds.[67, 68] Both techniques provide molecular structure and functional group identification of materials from their vibrational spectra. In the case of FTIR spectroscopy, the spectra reflect absorption of the incident broadband mid-infrared radiation when a given wavelength is resonant with a characteristic molecular motion of the sample. By comparison, Raman spectra are generated from the inefficient (typically one photon out of 10^6) inelastic scattering of incident monochromatic radiation, which gives a shift in wavelength reflecting the Raman active vibrational modes of the sample. In contrast to most of the analytical techniques discussed previously, FTIR and Raman spectroscopy uniquely allow for direct, non-destructive identification of unknown solid and liquid explosive samples with little to no sample preparation.

Recent instrumental developments in miniaturization and ruggedization have also led to a number of widely used field deployable instrument configurations.[67]

In the case of inorganic oxidizer analysis, Raman scattering and FTIR spectroscopy have both been demonstrated to be suitable analytical techniques for the identification of the characteristic anions of nitrates, chlorates, and perchlorates.[69, 70] Raman spectroscopy allows for non-contact, point-and-shoot analysis of oxidizer powders and can be used to sample these materials through translucent or transparent bags and containers. Some of the practical limitations of Raman spectroscopy include the potential for background fluorescence at the commonly used 785 nm excitation wavelength and challenges in analysis of darkly colored samples such as gunpowder or flash powders that may ignite under laser excitation.[13] FTIR spectroscopy does not suffer the same limitations and can often be used to facilitate analysis of samples that are problematic for Raman spectroscopy. Conversely, FTIR spectroscopy is highly sensitive to the presence of water and is typically not appropriate for analysis of water solutions or wet samples. The two techniques are complimentary in the information they provide, and recent trends suggest combining both in a single instrument configuration for maximum analytical flexibility. Finally, both techniques benefit from the presence of extensive chemical libraries (20,000 + compounds), which allow identification of not only various inorganic oxidizers but also conventional explosives, drugs, toxic industrial chemicals and common materials. However, identification becomes more challenging from mixtures.

The use of both FTIR and Raman spectroscopy coupled with imaging in laboratory scale instruments provides the analytical capability for chemical analysis of spatially distinct regions (particles of explosives, for example) at single particle sensitivity.[71] However, Raman and FTIR spectroscopy systems in portable or handheld formats are generally not considered to have the

sensitivity required for trace chemical analysis and are most often successfully utilized for direct analysis of small bulk (*i.e.*, visible but not easily weighed) amounts of unknown powder materials.[72] Future and ongoing developments for fieldable spectroscopic analysis of trace levels of inorganic oxidizers highlight the importance of developing new sampling methodologies compatible with wipe-based sample collection along with enhancements in sensitivity. Arnó *et al.* demonstrated a handheld FTIR spectroscopy platform using a diamond attenuated total reflectance (ATR) sampling system that required the user to place a small amount of an unknown powder or liquid sample in uniform contact with the ATR probe. To facilitate direct swipe sampling of trace surface contamination a non-infrared active sampling wipe was used with subsequent ATR analysis.[73] Compared to FTIR, Raman spectroscopy has many attractive features for trace inorganic analysis, but it does suffer from limited sensitivity due to the low Raman scattering cross section. One widely used approach for increasing the Raman scattering signal is surface-enhanced Raman spectroscopy (SERS).[74] Pilot *et al.* published a recent review on SERS, a technique where the analyte molecules are adsorbed onto a suitable surface, such a nano textured or nano particles of gold or silver. The surface creates a plasmon that is coincident with the exciting laser light leading to enhancement in the Raman scattering, often by as much as a factor of 10^5 - 10^6 .[75] Liszewska *et al.* demonstrated trace explosives detection from a range of SERS substrates using handheld Raman systems.[76] One operational limitation is that the sample must be dissolved in an appropriate solvent before deposition on the SERS active substrate. Additional efforts are focused on development of substrates that are suitable as both SERS substrates and collection wipes.[77] Recently, the application of direct swipe sampling of inorganic oxidizers with SERS analysis has been demonstrated. Chen *et al.* incorporated the diethyldithiocarbamate-induced formation of positively charged silver nanoparticles into a SERS substrate for the detection of

nitrate and perchlorate anions.[78] Alternatively, Liu *et al.* immobilized silver nanoparticles onto polyurethane sponge, creating an efficient swipe sampling SERS substrate for the detection of nitrate, chlorate, and perchlorate (Figure 6).[79] Given the difficulties with scanning large areas, novel combinations of swipe sampling and SERS substrate demonstrate a potential avenue for trace inorganic explosives detection.

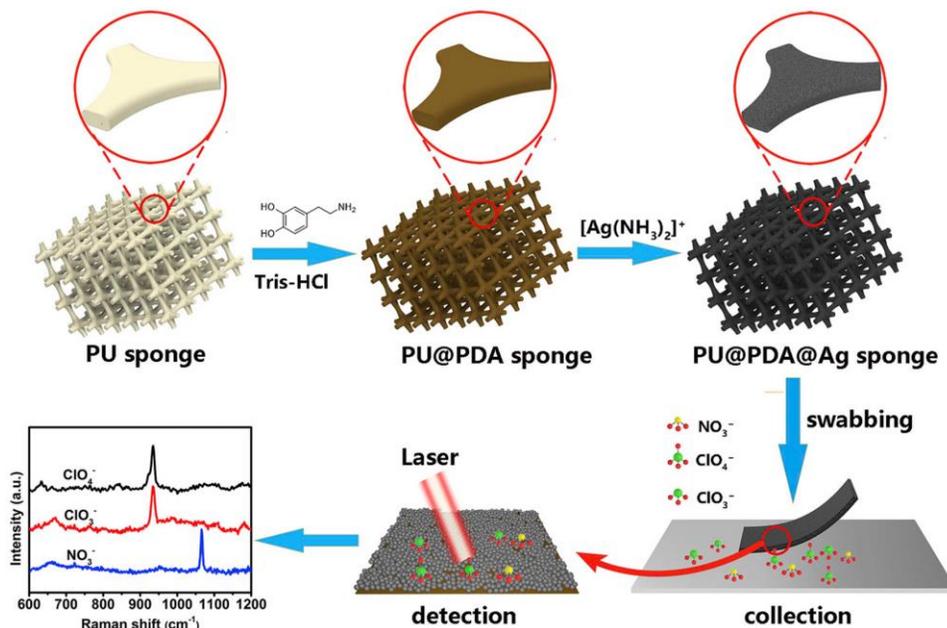


Fig. 6. Schematic representation of silver nanoparticles immobilized on polyurethane sponge through polydopamine reduction for use as wipe material for inorganic oxidizer SERS detection. Reprinted from reference [79] with permission from Elsevier.

5. General Discussion and Future Prospects

The chemical analysis of inorganic species and complex mixtures have long been demonstrated by a range of laboratory-based analytical techniques. Nevertheless, translating these established methods to fieldable trace explosives detection applications presents a number of hurdles. Many of these hurdles arise from the instrumental needs for rapid analysis, minimal or no sample preparation, suitable SWaP requirements, and overall system cost. Technologies and methodologies established for the detection of organic explosives face key challenges when

applied to inorganic fuel-oxidizer mixtures. For example, traditional analytical techniques for screening environments, such as thermal desorption IMS and MS, remain challenged by the refractory nature of inorganic oxidizers. Current work in high temperature desorption and reagent acidification provide potential solutions to this limitation, while still maintaining the ability to screen for a variety of other threat materials using the large base of already deployed systems. At the same time, many other promising approaches are being pursued, each having specific limitations and advantages depending on the required concept of operations and the type of information needed (*e.g.*, screening, attribution, quantification, trace vs bulk).

As pointed out in the introduction, it can be assumed that inorganic oxidizers will not be encountered in isolation. At a minimum, they will be mixed with a fuel and may contain many other species from the environment. Much of the current technology described in the literature is focused on analysis of pure inorganic oxidizers. To be a useful and deployable technology, any new technology must be able to detect the inorganic oxidizers in the presence of a complex chemical background. Instruments and sensors that continue to enhance selectivity either analytically or through advanced alarm algorithms will be best positioned to address these mixtures. Technologies like colorimetry and capillary electrophoresis have shown promise for specific targeted detection of inorganic species. Nevertheless, relevant technologies for screening and forensic investigations will benefit from maintaining capabilities necessary for the detection and identification of a variety of threat materials in addition to inorganics. These include conventional explosives, precursors, illicit narcotics, chemical warfare agents, and toxic industrial chemicals among others. Emerging techniques that have the flexibility to look for multiple species or are amenable to coupling with another detection technology in an orthogonal fashion would present appealing capabilities. Finally, trends demonstrating reduced SWaP and cost for portable

embodiments of more powerful analytical techniques such as MS (*e.g.*, higher mass resolution or MS/MS capabilities) or coherent anti-Stokes Raman spectroscopy present potential enhanced capabilities.

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Notes and References

† Certain commercial equipment, instruments, or materials are identified in this article in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by NIST, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

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