

Developments in Explosives Characterization and Detection

Marilyn Tourné*

Department of Chemistry, Tuskegee University, USA

Abstract

The continuous upsurge in terrorist activities makes it necessary to rapidly, efficiently, and reliably understand, detect, and/or prevent explosive threats. As such, intense research efforts continue to improve methods of detection and characterization of explosives through development of novel approaches and/or improvement of existing ones. This is especially true for home-made and/or improvised explosives devices. These next-generation threats require detection methods that will be sensitive and selective to a wide variety of traditional and non-traditional explosives and should be applicable in numerous detection scenarios. This review attempts to outline recent developments in the detection and characterization of explosives.

Keywords: Explosives detection; Explosives characterization; Explosives analysis; Analytical instrumentation; Review

Abbreviations: CL-20: Hexanitrohexaazaisowurtzitane; DNT: Dinitrotoluene; HMX: Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; HNS: Hexanitrostilbene; ONT: Orthonitrotoluene; PBX: Plastic-Bonded Explosive; PETN: Pentaerythritol tetranitrate; RDX: Cyclotrimethylenetrinitramine; TATB: Triaminotrinitrobenzene; TATP: Triacetone triperoxide; TNP: 2,4,6-Trinitrophenol; TNT: Trinitrotoluene; AE: Acoustic Emission; AFAI: Air Flow Assisted Ionization; AFM: Atomic Force Microscopy; APCI: Atmospheric Pressure Chemical Ionization; CMOS: Complementary Metal Oxide Semiconductor; CT: Computed Tomography; DART: Direct Analysis in Real Time; DBDI: Dielectric Barrier Discharge Ionization; DESI: Desorption Electrospray Ionization; DIC: Digital Image Correlation; EGDN: Ethylene Glycol Dinitrate; ELDI: Electrospray-Assisted Laser Desorption Ionization; E/N: Electric Field; FAIMS: High-Field Asymmetric Ion Mobility Spectrometry; FIB: Focused Ion Beam; FT-IR: Fourier Transfer Infrared; HePI: Helium Plasma Ionization; HMD: Home-Made Devices; IED: Improvised Explosive Device; IMS: Ion Mobility Spectrometry; IR: Infrared; ITMS: Ion Trap Mass Spectrometry; LCMS: Liquid Chromatography Mass Spectrometry; LIBS: Laser-Induced Breakdown Spectroscopy; LOD: Limit Of Detection; m/z : Mass to charge ratio; MEMS: MicroElectroMechanical Sensors; MIS: Molecularly Imprinted Silica; MS: Mass Spectrometry; MS/MS: Tandem Mass Spectrometry; NO_2 : Nitro-based compounds; PCA: Principle Component Analysis; PTR-MS: Proton Transfer Reaction Mass Spectrometry; QCL: Quantum Cascade Laser; QCM: Quartz-Crystal Microbalance; SANS/USANS: Small and Ultrasmall Angle Neutron Scattering; SAW: Surface-Acoustic Wave; SEM: Scanning Electron Microscopy; SERS: Surface-Enhanced Raman Spectroscopy; SPE: Solid-Phase Extraction; SPME: Solid-phase microextraction; SWNT: Single-Walled Carbon Nanotube; THz: Terahertz; TOF: Time-of-Flight; UV: Ultraviolet; vdW: van Der Waals

Introduction

Advances in technology to improve the sensitivity, selectivity, and reliability of analytical instrumentation for the detection of explosives have increased dramatically, particularly after the World Trade Center attack in New York City on September 11, 2001. Fortunately, these efforts have helped researchers expand the list of detectable, non-traditional, explosive substances. A large number of standoff distance methods have also been developed as a result of global terrorism acts such as the use of improvised explosive devices (IEDs) in both suicide and road side bombings. These developments in both existing and new

analytical techniques have enabled faster, more sensitive, and simpler determinations to facilitate the detection of explosives. Yet, because these threats become more dynamic and complex through variety of explosive materials utilized, cleverness of packaging, and variability of venue, the task of characterization and detection is still a huge challenge.

This review primarily focuses on recent developments in the detection of hidden explosives and the identification of suspect materials in post-detonation investigations. Characterization and detection methodologies applicable to traditional and non-traditional explosives will be highlighted. Emphasis will also be placed on detection methods involving trace, vapor, and standoff technologies. Only results published in peer reviewed articles will be discussed.

Traditional vs. Non-traditional Explosives

Traditional chemical explosives most commonly used by the military are composed of four elements: carbon, oxygen, nitrogen, and hydrogen. Some examples include 2,4,6-trinitrotoluene (TNT), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), pentaerythritol tetranitrate (PETN), and nitrocellulose. They are all nitro-based (NO_2) organic compounds. Nitration plays a big step in the manufacturing of these explosives. It is basically a substitution or double exchange reaction in which one or more NO_2 groups of the nitrating agent replace one or more groups (usually hydrogen atoms) of the compound being nitrated [1]. These explosive compounds are considered secondary (high) explosives because they cannot be detonated readily by shock or heat as with primary explosives. In other words, their detonation requires a shock produced by a primary explosive (such as lead azide, mercury fulminate, or tetrazene) [1]. Historically, the majority of explosive detection techniques focused on these traditional compounds since they were the ones mostly utilized in terrorist incidents.

Non-traditional chemical explosives are those which can produce

***Corresponding author:** Marilyn Tourné, Department of Chemistry, Tuskegee University, 301 Armstrong Hall Tuskegee, Alabama 36088, USA, Tel: 3347244532; E-mail: mtourne@mytu.tuskegee.edu

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similarly violent exothermic reactions but do not follow the classic compositions of military explosives such as IEDs, home-made devices (HMDs), slurry explosives, liquid explosives, plastic-bonded explosives (PBXs), emulsion explosives, or “green” explosives. Additionally, some newly synthesized energetic materials that contain more nitrogen than carbon by weight have shown desirable explosive properties [2-5]. The high nitrogen content of these novel compounds often leads to high densities, a quality which is known to liberate large amounts of energy from very small quantities of material. With the proliferation of technology and access to these innovative explosive substances, many terrorists have come to rely on them as a primary means of attack. These attacks have destabilizing and destructive results and are a primary issue for those nations facing terrorism threats. Many researchers understand this poses new challenges and, as such, have been exploiting promising new detection technologies for explosives. Some of those will be outlined in this review.

Characterization of Explosives

To fully characterize any compound a quantitative evaluation of its chemical, physical, mechanical, acoustic, thermal, and electromagnetic properties must be performed. The substance must undergo interrogation by a wide range of energy sources to study its responses and classify its limits and/or signatures. Successful characterizations of these compounds will help to improve their detection and facilitate any developments in sensing techniques.

Mechanical characterization of explosives–surface adhesion

The method of sample recovery for trace detection and identification of explosives plays a critical role in their detection. Traces can be searched for on large surfaces, on hands of suspects or on surfaces where the explosives were placed during preparatory phases (e.g. places where an IED was assembled, vehicles used for transportation, etc.) [6]. Contact sampling of explosives and explosive residues have been an area of much research in the past decade [7-15]. Swabbing methods have been somewhat successful at dislodging explosive particles from smooth surfaces but it remains a field deserving more research. The main drawback is the estimation, experimentally or theoretically, of the contact area between a particle and a substrate [16]. Zakon et al. [16] describes four main types of interactions that contribute to particle adhesion: electrostatic (if charges are present), van der Waals (vdW), chemical bonding, and capillary. Recently, Beaudoin et al. [17] investigated the vdW forces by mitigating capillary and electrostatic effects of several military explosives (TNT, PETN, HMX, and cyclotrimethylenetrinitramine (RDX)) against three coupons of aluminum alloys with three automobile surface finishes [17]. The force measurements were performed using colloidal probe microscopy (a form of atomic force microscopy, AFM) and simulated via a van der Waals force-based adhesion model and a composite effective Hamaker constant [18]. Their studies determined certain combinations of surface roughness led to particle-substrate orientations that produced extreme adhesion forces. Only after a full understanding of how explosive particles adhere to surfaces, will we be able to comprehend how to remove them from various substrates (smooth or porous).

Physical characterization of explosives–surface morphology

The surface morphology of energetic materials is vital to characterizing shock sensitivity and detonation properties [19]. Researchers have long been interested in developing explosives with insensitive properties for storage and transport purposes. A majority of the work in this area has focused on RDX and PETN, which are stable, crystalline high explosives [20-23]. Repeated investigations have shown

that much of our understanding on the mechanisms of initiation and detonation come from properties correlated to density [24-26], surface area [27], particle size [28-30], and crystal morphology [23,31,32]. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) has been used successfully to determine the surface morphology of triaminotrinitrobenzene (TATB), ammonium perchlorate, and PBXs [33-35] among many others. But more recently, Wixom et al. was able to provide morphology data, specifically porosity, of crystalline explosives using focused ion beam (FIB) nanotomography [22]. Despite being typically reserved for robust materials such as ceramics, semiconductors, and metals, FIB nanotomography was able to show porosity data in vapor deposited PETN and mechanically consolidated hexanitrostilbene (HNS). Their investigations provide accurate local measurement of density, which is known to affect explosive performance. In 2010, Stoltz, Mason, and Hooper were able to show the first small and ultrasmall angle neutron scattering (SANS/USANS) measurements on the internal void morphology of RDX powders [36]. SANS/USANS allowed them to characterize the internal void features on 10 Å–20 µm length scales. Neutron scattering is able to reveal clear differences between samples that offer a direct link between structural features and sensitivity testing. Other recent work has involved the tailoring of surface morphology in an attempt to characterize specific properties of energetic materials [37,38]. In 2012, Wang et al. were able to prepare ultrafine hexanitrohexaazaisowurtzitane (CL-20) by an ultrasound- and spray-assisted method [39]. Their studies determined the impact sensitivity of the prepared ultrafine CL-20 was significantly reduced as well as its critical explosion temperature (from 235.6 to 229.0°C). The decrease in critical explosion temperature indicates a lower thermal stability for the prepared CL-20 when compared to un-prepared (raw) CL-20. Morphology data is vital since it allows the determination of many properties including shelf life, vapor pressure, and density, among others. Being able to tailor these properties will aid researchers in understanding the sensitivity and detonation parameters of existing formulations and even influence the downstream development of future ones.

Thermal characterization of explosives–thermal and mechanical excitation

It is well documented that the vapor pressures of many explosive materials are highly dependent on temperature and may be substantially raised by minor temperature increases [40]. Studies utilizing mechanical excitation to induce heating in energetic materials have also been well documented [41,42]. In 1976, Loginov et al. [41] showed explosives such as RDX and lead azide were driven to initiation by applying low frequency mechanical vibrations. Theoretically, these techniques could be utilized as stand-off detection methods if, for example, heating of the target explosive could be achieved via an external source, such as ultrasonic radiation [43,44]. Despite this potential, only a few researchers have investigated these properties thoroughly. Mares et al. just recently explored the thermal and mechanical responses of PBX 9501 (a plastic-bonded HMX-based explosive) and two mock materials under mechanical excitations (ultrasonic) in the range of 50 kHz to 40 MHz [45]. Their observations showed a dominant mechanical resonance near the 200 kHz region. They were able to conclude that the active mechanism(s) causing heat generation under mechanical excitation are clearly dependent on the excitation frequencies used. In other recent work, Kovalev and Sturm demonstrated that local heating (so-called *hot spot formation*) on the surface of 2,4,6-trinitrophenol (TNP) single crystals occurred by direct mechanical insult from an AFM tip [46]. Despite the fact that preliminary mechanisms of decomposition are yet not firmly established, strong experimental evidence favors the *hot*

spot formation model [47-50]. In short, when an energetic material is exposed to focused weak insults (e.g., mechanical excitations), the mechanical energy is converted into heat, which is concentrated in a small area. Exploring these processes further will help us understand the origin of induced chemical decomposition as well as the detonation of energetic materials.

Acoustic characterization of explosives–damage determination

As mentioned previously, the storage and transportation of explosives has been an area of much research due to the materials being prone to damage and degradation. Thus, the inspection of damage evolution is vital for the characterization and development of new energetic materials. Previously, direct observation techniques such as SEM [51], computed tomography (CT) [52], and acoustic emission (AE) [53] have been used to evaluate the damage undergone by PBXs. Atomic emission allows continuous and real-time data acquisition but the spatial distribution of the damage is difficult to identify. Work done by Wang et al. incorporated whole field photomechanic methods, such as Digital Image Correlation (DIC) [54], and AE to help reveal full field damage distribution on uniaxially compressed PBXs. They found a *dominant localization band* which is believed to play a key role in the fracture of PBX explosives. It was proposed that this band was essentially the main reason for its non-linear behavior and damage evolution. Having a base understanding of non-linear structural mechanics of energetic materials will help reduce the microscopic fractures and failure mechanisms that govern the macroscopic mechanical behavior of these compounds.

Electromagnetic characterization of explosives–terahertz responses

Since the 1990's terahertz (THz) spectroscopy has found widespread applicability in areas ranging from condensed matter physics to the three-dimensional imaging of molecular solids [55]. The history and principle of this technique is described elsewhere [55-57] but, in short, THz spectroscopy covers the spectral range from approximately 3 cm^{-1} to 600 cm^{-1} , also known as the far-infrared (far-IR) region of the spectrum. Many materials, including explosives, have distinctive THz absorption features that are directly related to their crystal structure. Recently, the development of THz pulsed spectroscopy, using ultra-short pulses of coherent THz radiation, has greatly facilitated experimental access to this range of the electromagnetic spectrum [58]. A number of applications in recent years have demonstrated the use of THz spectroscopy in detection of explosives [59-63], giving additional information on the electro-magnetic responses of these materials. Specifically, Etayo et al. [64] performed a THz spectral characterization on a number of explosives (bullet gunpowder, mine gunpowder, PETN, TNT, and RDX) and was able to obtain refractive index, absorbance, and complex permittivity data on each [64]. The quantitative understanding of the electromagnetic responses of these materials will not only address the current need for better stand-off detection techniques, but will also help to provide a more complete characterization of these compounds.

Sampling Methods

As mentioned earlier, sampling is one of the most critical aspects of explosives detection. Several contact and non-contact sampling techniques have been developed throughout the years to help overcome the fact that vapor phase concentrations of most explosives are very low. As such, most common sampling methods utilize some form of preconcentration procedure such as vapor concentration. Types of sampling methods discussed in this section are surface (contact) sampling and remote (non-contact) sampling.

Preconcentration techniques

The preconcentration process of a gas may consist in adsorbing a target gas onto a specific adsorbent. This concentration step is followed by thermal desorption, allowing the generation of higher concentrations for the target compound [65]. Vapor concentration methods, such as solid-phase microextraction (SPME) [66-68], have been widely described in literature and have shown promising results with high explosives. Although, recent studies have focused on the development or appropriate selection of adsorbents for the preconcentration of explosives [69]. For example, Mohsen et al. was able to characterize textural properties of orthonitrotoluene (ONT) in an attempt to better understand the adsorption behavior of a hydrophobic zeolite and a porous activated carbon [65]. Similarly, Mattarozzi and colleagues developed a novel diethoxydiphenylsilane-based coating for planar SPME and were able to achieve quantitation limits in the low nanogram level [70]. Liquid concentration methods, such as solid-phase extraction (SPE) [71-73] have also been widely used in the detection of explosives. In 2011, Sun et al. [73] was able to use on-line SPE coupled to liquid chromatography mass spectrometry (LCMS) for the analysis of explosive residues in water [73]. Their results showed detection limits ranged from 0.05 to 0.5 $\mu\text{g/L}$ when 4000 μL of sample was preconcentrated onto the column.

Other studies have strived to develop and optimize the current instrumentation available for preconcentration [74]. One illustration is the development of an online SPE using molecularly imprinted silica (MIS) sorbent coupled with reversed-phase chromatography for the simultaneous extraction of commonly used nitroaromatic explosives [75]. The developed procedure by Lordel-Madeleine, Eudes, and Pichon was able to obtain high selectivity with extraction recoveries higher than 90% on the MIS sorbent. Beer, Müller, and Wöllestein were able to design and test an electrostatic particle precipitator on samples of dinitrotoluene (DNT) [10]. Their sampling system collected and concentrated trace amounts of analyte on a small substrate and was subsequently separated into high and low electron affinity fractions. High electron affinity fractions were then collected, desorbed, vaporized, and detected. The optimizing or re-designing of preconcentration sorbents and/or instrumentation will improve sampling performance and recovery of explosive vapors and provide analytically reliable measures of the sample in question.

Surface sampling techniques

A common surface sampling technique that has been investigated for many years has been the swabbing of explosive residues [6,7,9,11,76-78]. Important issues faced by this methodology were described in the section "*Mechanical characterization of explosives–surface adhesion*". More novel contact sampling schemes involve an electrostatic precipitator as mentioned in the section "*Preconcentration techniques*" [10] and solid-state voltammetry (*forensic finger*) [79]. Bandodkar et al. [79] were able to develop a wearable fingertip sensor for the rapid on-site square-wave anodic stripping voltammetric screening of explosive surface residues. The *forensic finger* is equipped with electrodes (screen printed on a stretchable finger cot substrate) and complimented with a conductive, ionogel electrolyte. Target analytes are mechanically transferred onto the electrode surface via swiping the sensor over the area of interest. Even though the authors did not publish detailed quantitative information, it is clear this wearable forensic finger holds considerable promise as a portable screening method for the rapid identification of explosives.

There is also a number of ionization sources that have been

introduced that only need be in the proximity of the sample. Some examples include laser-induced breakdown spectroscopy (LIBS) [80,81], desorption electrospray ionization (DESI) [82,83], direct analysis in real time (DART) [84], paper spray ionization [85,86], thermal desorption [87,88], low-temperature plasma probe [89], atmospheric pressure dielectric barrier discharge (DBDI) [90], and electrospray-assisted laser desorption ionization (ELDI) [91], among many others.

Remote sampling techniques

Remote sampling of explosives is extremely challenging because, as discussed previously, most of them have very low vapor pressures, which severely reduces the number of gaseous molecules available for sampling. Over the years, devices have been developed to improve the design, efficiency, selectivity, and sensitivity of remote (non-contact) sampling [92-95]. One example given by He et al. [96] is the investigation of an air flow assisted ionization (AFAI) method developed for ambient mass spectrometry [96]. The AFAI method was able to transport TNT ions over long distances due to its high flow rate air flow extraction. In 2012, Yang, Pavlov, and Attygalle were able to sample TNT vapors placed 5 m away from a mass spectrometer using Helium plasma ionization (HePI) [97] and in 2013, conjugated polymer networks were used by Gopalakrishnan and Dichtel to detect RDX vapors [98]. They reported that trace amounts of RDX, in either solution or vapor phase, were able to quench the fluorescence of a cross-linked phenylene vinylene polymer network. The polymer network was shown to also respond to traces of TNT and PETN. As another example, Takada et al. [99] worked on the development of a high-throughput portal system which employs the use of a push-pull vapor sampler. The sampler, which is coupled to an atmospheric pressure chemical ionization (APCI) source and an ion trap mass spectrometer (ITMS), was designed to be installed in an automated ticket gate of a train station. False-positive rates were evaluated for the portal system and field tests were performed. Authors report being able to sample and detect high throughput (e.g., 1200 persons/hour) vapors of triacetone triperoxide (TATP). The success of sampling methods based on fluorescence quenching [99-101], portal technologies, or others, especially those that do not require preconcentration, should find great use in non-proximate sampling of explosives and explosive residues.

Detection of Explosives

Historically, a great number of articles, books, reviews, and conference proceedings have provided extensive discussions about individual modes of explosives detection. Even though numerous advances have been made in recent years, the *ideal* detector has yet to be found. Each scenario (remote vs. contact, trace vs. bulk, etc.) presents a whole new set of challenges for researchers. The goal has always been the same: develop faster, more sensitive, less expensive and simpler detectors that will facilitate the identification of explosives. This task is not trivial and changes with every new threat. As such, much focus has been placed on developing and integrating suites of detection schemes that could handle both traditional and non-traditional energetic compounds. This section will attempt to summarize the most recent advances in explosive detection technology.

Mass spectrometry

Mass spectrometry (MS) in various forms (quadrupole [102,103], ion trap [88,104], time-of-flight (TOF) [105,106], tandem-based (MS/MS) [107,108], and hybrids) have been used for the detection of energetic materials due to its selectivity, sensitivity, reliability and

speed; it is a proven technology. It would not be an overstatement to cite MS as a major contributor to the technology that makes it possible for scientific experts to monitor and detect explosives and explosive residues. Briefly, classifications of compounds in MS are performed first by ionization succeeded by their separation based on mass-to-charge (m/z) ratios. Historically, two major disadvantages of MS have been its size and cost. Consequently, major progress has been made in miniaturizing MS instruments [109-112] which, in turn, reduces cost. For example, Chen et al. [113] recently developed a miniature rectilinear ion trap for the detection of several organic and inorganic explosives [113]. Their explosive detection platform also consisted of a halogen lamp, which aided in acquiring limits of detections in the picogram range (e.g., 10 pg for TNT; 20 pg for RDX). Other research has focused on increasing the levels of confidence (decreasing rate of false positives) for explosive detection [114]. By utilizing proton transfer reaction mass spectrometry (PTR-MS), Sulzer and colleagues were able to observe an unusual bias in the detection sensitivity of TNT on the reduced electric field (E/N). The signal of a protonated TNT molecule was observed to initially increase with increasing E/N (the usual behavior is for the signal to decrease). The authors attributed this behavior to ion-molecule chemistry occurring in the drift tube and further stated it could be used as a measurable signature to reduce false positives.

Ion mobility spectrometry/high-field asymmetric ion mobility spectrometry

In traditional ion mobility spectrometry (IMS), sample is introduced into a reaction region where ions are formed. A narrow pulse of ions is injected into a drift region and move along this drift tube with the aid of an applied electric field (1-500 V/cm). In the drift region, ions are separated based on their low-field mobility, which is dependent on their charge and size. The IMS technique is able to operate at atmospheric pressure and room temperature. Thus far, IMS, formerly known as plasma chromatography, has been most widely used for explosives monitoring because of its high sensitivity and amenability to miniaturization [115]. However, a major disadvantage of IMS has been its limited selectivity, such that some interferent ions have the same low-field mobility as the analyte ion, and thus can result in a false positive. During the last decade, IMS research has exploded and, as such, has experienced much progress in the selectivity and resolution of explosives detection. For example, Davis et al. observed a dramatic improvement in resolving power values for a stand-alone IMS with the increase of buffer gas pressure [116]. When operated at a pressure of 2.5 atm, authors reported a resolving power of 102 as well as an increase in peak-to-peak resolution. Additional work to enhance the resolution of IMS instruments has been performed by Du et al. [117]. Through the use of SIMION simulation, they established a simple space compression-dispersion model for ion transport in IMS. The model characterized the Bradbury-Nielson gating electric field into 3 zones: the depletion zone, the dispersion zone, and the compression zone. They verified the theory by monitoring the influences of gating voltage on the full width at half-maximum of the analyte peak. The measured resolution was raised from 18 to 33 by increasing the gate voltage difference from 50 V to 350 V. Other parameters that have been investigated to enhance its performance include ionization sources [118-120], solvent effects [121], buffer gases [122], ion trajectories [123], and coupling techniques [124,125]. Potential methods to improve the selectivity, sensitivity, and resolution of IMS will ensure its continued success in the monitoring and detection of energetic materials.

High-field asymmetric ion mobility spectrometry (H-FAIMS, or more commonly FAIMS) is an ion mobility technique that also operates

at atmospheric pressure and room temperature to separate gas-phase ions. Although, separation of the ions is based on high-field mobility and occurs by applying a non-constant high electric field ($>10,000$ V/cm) that alternates between high and low voltages of opposite polarities. Over the course of its development, the geometry of the separation cell (based on a pair of analytical electrodes) has diverged into two different pathways: (1) a pair of flat planar electrodes and (2) a pair of cylindrical (or curved) electrodes [126]. The geometry of a FAIMS cell is very important and has been shown to affect signal transmission, resolution, and resolving power [127,128]. In 2011, Rorrer and Yost investigated the effect of solvent vapor concentrations on four common nitroaromatic explosives [129]. Results showed that adding small amounts of solvent vapor to the drift gas dramatically improves the resolving power of isomeric ions. Some important innovations of FAIMS technology include miniaturization [130] and the optimization of waveforms [131].

Terahertz spectroscopy

As mentioned previously in the section “*Electromagnetic characterization of explosives-terahertz responses*”, THz spectroscopy has been successfully used to characterize the electromagnetic properties of explosives. This technology has also experienced much attention with the nondestructive detection of explosives and explosive content. One example explores using cutoff frequencies to recover spectral features lost by rough surface scattering [132]. The ability to recover the spectral features of rough dielectric materials from diffuse THz scattering may prove useful for the design of future security screening systems. Other studies report the use of general frameworks for numerical simulation of IED detection-based scenarios with density functional theory (DFT) calculations [133]. Only by understanding the molecular origin of the complex, low frequency modes obtained in the THz regime will researchers be able to identify the spectral signatures of explosive compounds.

Infrared spectroscopy

Spectroscopy-based techniques offer one of the most selective approaches for chemical identification from remote distances. In its various modalities (e.g., mid-IR, near-IR, Fourier Transform-IR (FT-IR)), infrared (IR) has been shown to be useful for the detection of explosives [134,135]. In direct measurement spectroscopic techniques, the use of a single optical beam obtains spectral features without altering the molecular structure of the residue. A major drawback of single beam technology is the requirement of a reference spectrum to remove background interferences. Recently, Morales-Rodriguez et al. reported the identification of RDX and PETN explosive residues from 8 meters away by using infrared (IR) and ultraviolet (UV) radiations [136]. The requirement of a reference spectrum was eliminated since the spectral information was obtained from a two beam technique. Other investigations performed by Castro-Suarez and colleagues were able to obtain high quality vibrational signatures of TNT deposited on aluminum plates by using FT-IR spectrometry [137]. Their technique, which employed gold-coated optics and a reflective telescope-coupled remote detection system, was able to identify TNT signatures anywhere from 4-55 meters away. Pacheco-Londoño et al. [138] were able to show the possibility of detecting the presence of peroxide-based explosives, such as TATP, as well as, nitroaromatic compounds when they are in the gas phase mixed with air [138]. Their methodology implemented FT-IR and quantum cascade laser (QCL) based dispersive IR spectroscopy. They showed limits of detection (LOD) values for TATP of 800 pg/m^3 and 300 pg/m^3 for FT-IR and QCL detection, respectively. Even better LOD values were obtained from FT-IR and QCL for 2,4-DNT of 31 pg/m^3 and 0.7 pg/m^3 , respectively. Current trends in IR spectroscopy

research show its versatility and make it an attractive candidate sensor for a variety of security related applications, including the screening and detection at remote distances.

Laser induced breakdown spectroscopy

Another example of a two beam spectroscopic method that does not require a reference spectrum is laser-induced breakdown spectroscopy. LIBS can determine the elemental composition of a compound from the light emission of laser-generated plasma on the basis of elemental and molecular emission intensities [139]. Recently, more attention has been placed on LIBS explosive research due to its standoff detection capabilities [140-143]. Recent and exciting work has been done by Lucena where they use LIBS to detect explosive-contaminated human fingerprints 31 meters away from the sensor [144]. The LIBS instrument, which was fitted with 2D scanning capabilities, was designed to capture spectral information from laser-induced plasmas of fingerprints that have been contaminated with chloratite, TNT, DNT, RDX, and PETN and deposited on aluminum and glass substrates. After evaluating the sensor performance for lateral resolution and data acquisition time, they determined scanning mode LIBS reached 100% sensitivity in fingerprint recognition. The possibility of scanning a surface by standoff technologies, such as LIBS, provides a promising alternative in terms of trace explosive detection.

Raman spectroscopy and surface-enhanced Raman spectroscopy

Raman spectroscopy offers molecule-specific information by measuring the vibrational, rotational, and other low-frequency transitions in a sample through the analysis of scattered photons that have been excited from a laser. Considerable work has been done in recent years with Raman spectroscopy to improve its portability and standoff capabilities for explosive detection. For example, Chung and Cho recently developed a standoff nanosecond-gated Raman detection system composed of a reflective telescope, a pulse laser, and a camera [145]. Experiments performed with TNT, RDX, and HMX displayed detection capabilities of up to 30 meters away. Authors noted that despite their ability to locate relevant peaks of compounds at a 30 meter distance, it was difficult to analyze the exact identity of the energetic materials. Other work performed by Stewart et al. explored the potential of a handheld Raman spectrometer to detect aqueous samples of hydrogen peroxide, which can serve precursor screening for TATP [146]. Even more recently, Hwang et al. reported rapid and sensitive recognition of 14 selected explosive compounds using Raman spectroscopy and principle component analysis (PCA) [147].

Historically, surface-enhanced Raman spectroscopy (SERS) was explored in an attempt to overcome the problems arising from low sensitivity in Raman spectroscopy. Nowadays, SERS is readily used in detection of explosives because of its high quality Raman spectra, low cost, and portability potential. In 2013, Botti et al. [148] applied compact SERS to detect and identify traces of PETN, ethylene glycol dinitrate (EGDN), RDX, and TNT [148]. Molecular identification was performed in only 10 s and explosive compounds were identified at trace level quantities, as low as 10 pg . Some investigations have been performed on SERS topics such as those to help with the amount of airborne particles reaching the detector (concentration) [149] and those that employ separation methodologies, such as liquid chromatography, before detection [150], but most of the literature describes the use of different substrates [151-153] to enhance its performance. Both Raman and SERS complement IR spectroscopy as a method for obtaining vibrational information on the target analyte.

Sensors

Sensor technology has shown considerable promise in the field of explosive trace detection since they are generally highly sensitive, small in size, autonomous and inexpensive. In particular, there have been several reports on microelectromechanical sensors (MEMS) such as metal oxide sensors [154], micromechanical resonators [155], quartz-crystal microbalance sensors (QCM) [156], and surface-acoustic wave (SAW) sensors [157]. Other common sensing modalities for the detection of explosives include fluorescent [158], luminescent [159], and electrochemical [160] techniques.

Carbon nanotube-based sensors have also been investigated because they seem to exhibit faster response times and have higher sensitivities [161]. Carbon-based materials such as diamond, carbon nanotube, and graphene possess excellent properties (low mass, high thermal conductivity, hydrophobic surface, and tailorable electronic configuration) that make them especially suitable for MEMS applications [162]. Despite the attractiveness of using carbon-based materials as sensors, it must be noted many vapors or gases may become adsorbed onto the nanotubes, causing a change in their resistance [163]. As such, much research has been dedicated to functionalizing the surface of the material in order to increase the affinity towards a specific analyte. In 2013, Liu [164] presented a novel complementary metal oxide semiconductor (CMOS) integrated with a DNA-functionalized single-walled carbon nanotube (SWNT) nanosensor as a compact, portable, and miniature sensing system for explosives detection [164]. The responses achieved from the DNA-SWNT to DNT vapors increased by 23% compared to a non-functionalized SWNT. Sensor technology promises to provide a broad range of novel uses and improved technologies.

Canines

Trained canines have been deployed successfully for explosive demining purposes since World War II [165]. To this day, canines are still considered the gold standard for field methods of detecting explosives. The amount of explosive vapors available to a trained canine depends on the amount of material, container volume, explosive vapor pressure, and temperature [166]. The canine LOD varies somewhat with the compound being detected, but it is nominally in the parts-per-billion (ppb) to sub-ppb by volume range at atmospheric pressure conditions. Research has shown that dogs do not rely on vapor signatures from the pure compound, but rather a combination of odors from solvents, synthetic remnants from the manufacturing process, and degradation by-products [165]. Published work by Almirall et al. [167] has reported the identification and characterization of odor chemicals emanating from explosive compounds [167,168]. Continuing research in canine olfaction and development in improved training aids will ensure the use of canines in explosives detection for many years to come.

Conclusion

It is clear the field of explosives detection and characterization is a dynamic one with new challenges presented daily. Characterization efforts mainly focus on providing detailed information on the fundamental properties (chemical, physical, mechanical, acoustic, thermal, and electromagnetic) of explosive compounds. Detection efforts focus on finding the most efficient and accurate method with the least human intervention. To this end, many developments have been made in recent years for remote sampling and detection. Detection schemes at the molecular level help to provide researchers with a wide variety of analytical techniques. In order to improve the design of

viable detection systems even further, stronger focus must be placed on expanding the knowledge of molecular and spectroscopic properties. This review has focused on the recent developments of characterization and detection methods for explosives and explosive residues.

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