Advances in Explosives Analysis – Part II –Photon and Neutron Methods

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Abstract

The number and capability of explosives detection and analysis methods have grown dramatically since publication of the Analytical and Bioanalytical Chemistry special issue devoted to Explosives Analysis [1]. Here we review and critically evaluate the latest (the past five years) significant advances in explosives detection, with details about the improvements over previous methods, and suggest possible avenues towards further advances in e.g., stand-off distance, detection limit, selectivity, and penetration through camouflage or packaging. The review consists of two parts: Part I discussed methods based on animals, chemicals (including colorimetry, molecularly imprinted polymers, electrochemistry and immunochemistry), ions (both ion mobility spectrometry and mass spectrometry), and mechanical devices. This Part II will review methods based on photons, from very energetic photons such as X-rays and gamma rays down to the terahertz range, as well as neutrons.

Keywords: Explosives detection, trace analysis, explosives, improvised explosives, instrumentation, reviews

Introduction

Part I provides a more complete introduction to this review [Brown KE, Greenfield MT, McGrane SD, Moore DS (2015) Anal Bioanal Chem doi:10.1007/s00216-015-9040-4] This Part II will highlight many of the newest and most capable explosives detection and analysis capabilities that utilize photons to interrogate the sample. Also included are methods using neutrons. We include a number of exciting new stand-off detection developments at 100 meter distances and beyond. Our principal focus will be on archival scientific literature, rather than vendor information, in order to concentrate on the scientific principles and advances rather than commercial off the shelf (COTS) embodiments, except in selected cases. The recent shift in predominant usage from military explosives to homemade explosives (HME) has driven significant changes in detection methodologies, particularly to differentiate threats from benign usage (such as farming) of HME components.

Methods Using Ionizing Radiation or Neutrons

X-ray diffraction:
X-ray diffraction (XRD) of a sample provides crystalline structure information. It is a promising non-invasive, non-contact method to detect and identify liquid and solid materials [2,3]. In energy dispersive (ED) XRD a polychromatic X-ray beam is utilized to

probe the photon-matter interactions of coherent scattering, in the sample. An energy resolved detector at a fixed scattering angle measures the material specific spectrum. The specificity of the spectrum is due to the atomic planar spacing (d) and radiation wavelength (λ) of the material according to Bragg's law ($2d\sin\theta=n\lambda$, n is an integer). Alternatively, as in angle dispersive X-ray diffraction (AD-XRD) one can keep λ fixed and vary θ [4]. These isomorphic detection techniques are most applicable to TSA or detection portals as the equipment is non-portable due to size and shielding requirements.

Advantages of XRD over typical X-ray imaging techniques are covered in Well's comprehensive review from 2012 [3]. X-ray diffractive imaging devices are commercially available and their intrinsic features necessary for detecting solid and liquid explosives and inert materials are summarized by Harding [5]. Much work over the past five years has been in improving detectability through combining detection techniques,[4,6] analysis methods [7], and optimization of x-ray geometry [8-12] and detector geometry [11]. Combining AD-XRD and ED-XRD with a pixelated energy resolved detector requires no moving parts and short acquisition times (~ 1 second), when merged with principal component and discrimination analysis, to differentiate between inert materials and explosives such as Semtex and ammonium nitrate emulsions[6]. X-ray emission spectroscopy for future trace and small-scale bulk detection is being investigated, but with much less effort [13-15].

Neutron activation and gamma emission

Active neutron interrogation methods are used to identify the relative chemical content of certain elements (N, O, Cl, H) through their characteristic gamma ray emission, neutron scattering and neutron absorption. Abnormally high nitrogen content is typically used as a detection flag for an explosive. Neutron activation works well for high nitrogen explosives but not all explosives are nitrogen based such as the homemade explosives TATP and potassium chlorate plus sugar. Two main advantages of using neutron activation are the ability of neutrons to pass through high atomic number materials, such as metals, and the specificity to differentiate between organic and inorganic materials. The largest disadvantages are neutron sources produce harmful radiation doses if not shielded properly or at the correct stand-off and neutron interrogation can cause unwanted material activation.

There are five main neutron activation interrogation techniques: thermal neutron analysis (TNA), fast neutron analysis (FNA), pulsed fast thermal neutron analysis, fast neutron elastic scattering (NES), and neutron transmission/fast neutron radiography. A recent review in 2014 by Whetstone and Kearfott describes the basic principles behind each of these interrogation techniques and highlights their advantages and disadvantages as well as gives an overview of the different neutron sources currently used for each technique [16]. An alternative detection method suggests utilizing gamma rays to induce neutron scattering for detection[17].

Advances in this field revolve around fusion of different techniques, advances in neutron sources in terms of energy and portability, and increases in detection sensitivity. FNA, TNA and dual x-ray imaging were combined to analyze ratios of four common elements (Cl, H, Fe, N). Use of different ratios of the elements (e.g., N/H, Cl/H, Cl/N) was found to reduce the false alarm rate, and use of eight detectors in front and eight behind a container allowed location of a suspect

material (see Fig. 1) to within an area 0.4 x 0.4 m [18]. A tabletop 10 Hz thermal neutron generator for gamma spectroscopy has been developed in France using a dense plasma focus technique [19]. Scintillator development for TNA gamma emission detection was found to increase medium to large antitank landmine detection to a depth of 30 cm and horizontal displacement of 30 cm and allow for detection of moderate to large ammonium nitrate based IEDs (improvised explosive devices) in culverts [20]. Further experiments on IEDs and UXO (unexploded ordinance) suggest the gamma emission count time depends on a combination of the soil moisture, cladding thickness of the explosive containment and to a lesser extent the explosive composition [21]. Recent work by Batyaev measured and calculated gamma emission receiver operating characteristic (ROC) curves on explosives (TNT, Tetryl, NG, RDX) and benign materials and showed it was possible to estimate ROC curves [22].

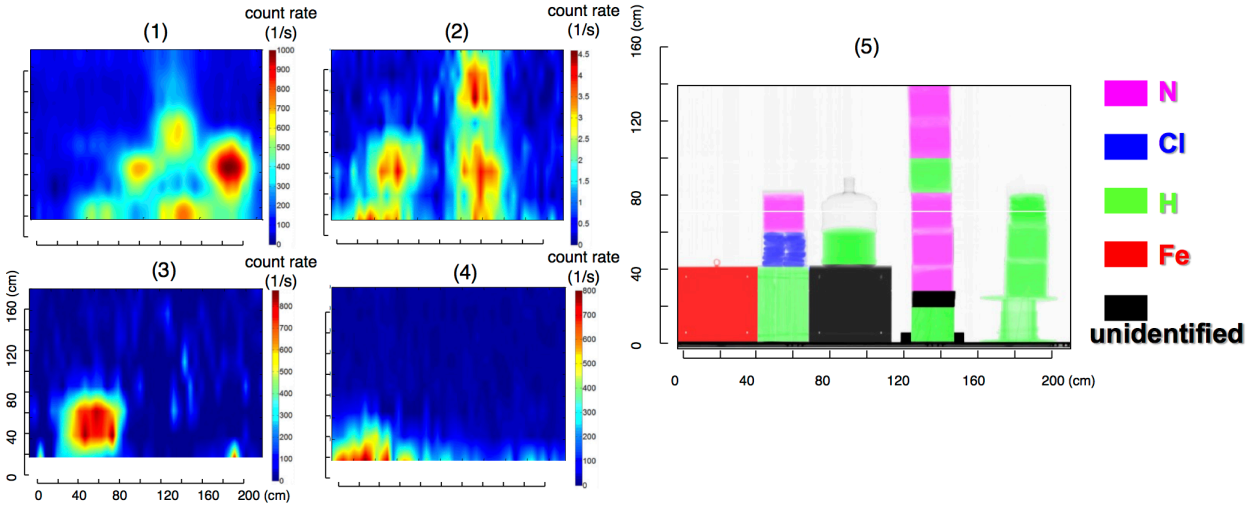

Figure 1. Two dimensional TNA elemental distribution of 1) Hydrogen, 2) Nitrogen, 3) Chlorine, 4) Iron and 5) the combined X-ray image with elemental distribution. From Ref. 18 used with permission.

Terahertz Methods

Terahertz spectroscopy and imaging

Terahertz (THz) spectroscopy (the spectral region is usually defined as frequencies from 0.5 to 10 THz, or wavenumbers from 15 to 300 cm^{-1}) and other long-wavelength spectroscopies (*e. g.* millimeter wave, GHz) probe the low energy modes of molecules and longer-range intramolecular modes, yielding another set of molecular "fingerprints" for explosives detection. One promising attribute of THz spectroscopy is its ability to penetrate and detect non-metallic items, a boon for detecting hidden or concealed objects. There is still a great deal of research being performed on obtaining the spectral signatures of various conventional and homemade explosives, as well as developing signal processing techniques for both spectroscopy and imaging schemes. There are few THz detection papers containing quantitative analytical metrics such as detection limit. The selectivity of the method is discussed in several papers, especially where it involves THz spectral signatures and their variation with sample type or matrix.

A common technique for THz spectroscopy is Time Domain Spectroscopy (THz TDS), a pump-probe method. A THz pump pulse (generated by an ultrafast laser) is sent through a sample to a detector, where it is combined with a shorter probe pulse from the laser. The THz electrical field can be recorded over a period of time, and can be Fourier transformed to a frequency spectrum. A great deal of research has been performed on the spectral signatures of explosives and related materials through THz TDS, including the conventional molecular explosives RDX, HMX, PETN, and simulant molecules [23-28]. Likewise, the spectral signatures of explosive mixtures and plastic compositions have been studied [29-33,26-28]. Additionally, spectral signatures of homemade explosives and related materials have been analyzed [34-36]. Stand-off detection using THz TDS, where the operator is physically separated from the sample, has also been investigated [31,25].

There are several challenges associated with THz spectroscopy for explosives detection, including interference from barrier or concealment materials (*e. g.* envelopes, clothing, etc.), surface roughness of the samples, and water vapor/humidity present in the air [37,30]. Many researchers have addressed these challenges through developing methods to separate spectral fingerprints of explosives from barrier materials [30,38,39,31,40], and signal processing algorithms to compensate for water vapor absorption [32].

THz imaging has been suggested to be a more viable option for explosives detection than spectroscopy, though subject to similar challenges [37]. Two common techniques in recent THz imaging research are passive imaging, where the system detects naturally occurring radiation in the THz frequency range, and THz reflection imaging, where chemical identification is possible. The research on passive imaging has largely focused on image processing for high-resolution images. Trofimov and coworkers [41,40,42], along with collaborators in China [43], have developed several sets of spatial filters to apply to the obtained images to detect hidden objects. The challenge of surface roughness in THz imaging has been addressed by Zurk and coworkers by a novel 3-dimensional imaging technique through a synthetic aperture and other methods [44-48]. Research to both detect and identify explosive objects has also been performed by several groups. Sleiman *et al.* used THz TDS for chemical mapping of RDX, PETN, and RDX/PETN mixtures [28]. Startsev *et al.* used a tunable optical parametric oscillator (OPO) to frequency raster-scan several explosives; the imaging analysis assessed the chemical composition of the materials studied (see Fig. 2) [49]. Palka *et al.* compared the THz transmission spectra of explosives by THz-TDS and an OPO-based system [50].

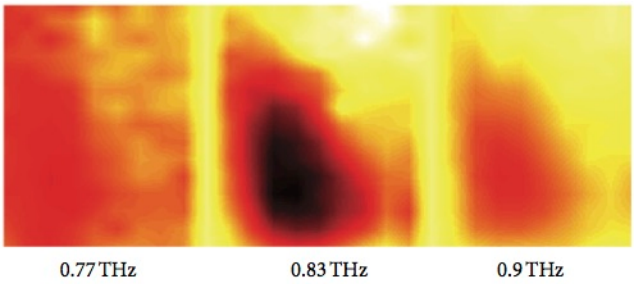

Figure 2. Raster scanned THz images of RDX concealed in a paper envelope with OPO tuned to 0.77, 0.83, and 0.90 THz. 0.83 THz is the frequency at the RDX resonance peak of width (FWHM Gaussian fit) of 0.13 THz. From Ref. 49 used with permission.

Researchers have coupled THz spectroscopy and imaging to other technologies. Carriere and coworkers [51-53] combined THz with Raman spectroscopy (THz-Raman®) for extremely low frequency (~5 cm^{-1}) Raman measurements of explosives. Lu et al utilized at flexible tube-lattice fiber probe combined with THz TDS for THz hyperspectral imaging[54]. Perov *et al.* developed a new THz imaging scheme based on a backward wave oscillator and heterodyne detector to detect concealed objects [55]. Simoens and coworkers have developed a microbolometer array prototype for explosives detection at two different frequencies [56,57]. Bolduc *et al.* has utilized a microbolometer-based THz imaging camera to detect a concealed plastic knife [58].

Vibrational and Electronic Spectroscopies

Infrared

Infrared (IR) absorption/reflectivity/attenuated total reflection (ATR) spectroscopies are powerful methods of explosive identification and detection via measurement of the vibrational spectrum. Portable devices that measure ATR spectra of unknown materials for identification by library matching are available from several commercial sources. ATR avoids the sample preparation traditionally involved in transmission IR measurements. Since infrared penetration depth for neat materials is on the order of a micrometer, trace amounts of solids or liquids (e.g., ng to μg) can be measured if they can be placed into contact with the ATR prism. Stand-off methods retain this sensitivity to trace residues while avoiding sampling.

Passive stand-off IR can utilize the thermal emission spectrum for identification. Long wave infrared (LWIR) at 8-14 μm wavelength is emitted as thermal radiation from a sample that is modulated by the spectrally dependent emissivity. This signal is typically detected by HgCdTe based sensors or microbolometer arrays through a Fourier transform infrared (FTIR) interferometer [59]. Coupled with an infrared sensitive focal plane array detector, FTIR hyperspectral imaging is capable of detecting and identifying trace amounts of explosives on surfaces (at ~$\mu g/cm^2$ levels) in 30 s [60-62]. LWIR can be used for thermal imaging without spectral resolution as a simpler, but less selective means of identifying spatial anomalies in an environment that may be hazardous [63]. LWIR systems are also often sensitive to mid wave IR (MWIR) light in the wavelength range down to 3 μm.

Active stand-off IR involves illumination with either a thermal source or a laser. While diffuse scattering of thermal IR sources off the sample can aid in spectral acquisition [60,59,64] the collimation and power on target for laser sources is far greater. Femtosecond optical parametric oscillators [65] and tunable carbon dioxide lasers [66] have been used as spectroscopic IR sources, but most research is currently focused on illumination by tunable quantum cascade lasers (QCLs). Active QCL illumination coupled with array detectors allows hyperspectral imaging that can match the spectrum of residues with library spectra of explosives (see Fig. 3) [67-70]. The backscattering collected is a strong function of the angle of incidence, but the contrast in spectral features has been observed to remain with orders of magnitude less signal than specular reflection [71,64]. QCLs have the resolution required to measure gases, as has been demonstrated in stand-off

diffuse reflection[72] and headspace monitoring cavity ringdown spectroscopies [73]. Multiple QCLs can be chained together to increase the spectral coverage [74].

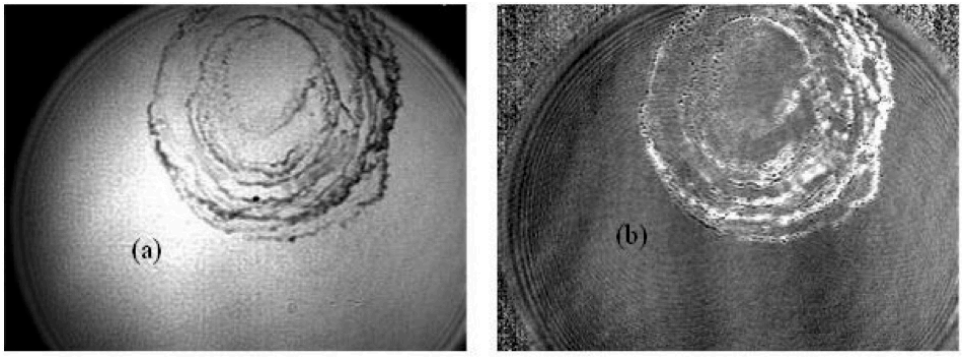

Figure 3: Active hyperspectral imaging of an RDX residue using QCL illumination and an uncooled microbolometer camera. Figure 3a is the brightfield image, and Figure 3b is the difference image showing bright areas of RDX residue cased by preferential absorption when compared to an off-absorption wavelength. Reprinted with permission from Ref. 69. © 2010 SPIE

It should be noted that IR spectra measured in emission or backscattering geometries often look different from those measured by transmission or ATR. The particle size, shape and environment can cause peaks to look absorptive, dispersive, or intermediate between the two [75,76]. This is a fundamental physical property that must be accommodated in spectral library match algorithms.

Short wave IR (SWIR) in the range 900-2500 nm offers more penetration ability than visible light and less expensive, more sensitive array detectors than are available at LWIR and MWIR. While molecular vibrations absorb in the MWIR and LWIR, overtone (excitations of multiple vibrations) absorptions can be observed in SWIR. The spectroscopic determination of materials is less decisive, but the experimental implementation is simpler, smaller, and less costly. These advantages have spurred numerous implementations of SWIR hyperspectral imaging for explosives detection and identification. Discrimination among similar explosives imaged in handprint residues was demonstrated [77,78]. A dual SWIR and Raman hyperspectral imager on an unmanned ground vehicle was shown to enhance explosive discrimination by coupling both methods [79]. A supercontinuum extending from 1300-4300 nm was used to measure diffuse reflectance spectra of several HE over a range extending from SWIR to MWIR [80].

Ultraviolet/Visible

Detection and identification of explosives based on reflectivity in the ultraviolet to visible ranges have not been as thoroughly researched as other methods. Since the underlying physics relies on electronic absorptions that are typically broad and indistinct, selectivity is not expected to be nearly as high as for vibrational spectroscopy. Despite these difficulties, differential hyperspectral imaging [81,82] under active illumination in the 200-500 nm range has been used to achieve a limit of detection of 100 ng for TNT with selective ROCs [83].

Luminescence

Traditionally, chemiluminescence-based explosives detectors consist of a polymeric fluorophore that has some binding selectivity toward the explosive molecule [84]. Once bound, the fluorescence is quenched. This method has been used commercially in the Fido® detector (FLIR Systems, Inc.). Recent research in chemiluminescence explosives detection has been focused on novel fluorescent materials and other luminescence schemes, including electrochemiluminescence and upconversion luminescence.

Novel materials for chemiluminescence-based explosives detectors include metal-organic frameworks (MOFs) and various polymer and photonic crystal films. Hu published an excellent review on the mechanisms and research into metal-organic frameworks for small molecule detection [85]. Xu *et al.* developed a nanoscale MOF to detect nitroaromatics in ethanol [86], and Wu et al utilized a MOF for carbon disulfide and nitrobenzene detection [87]. Ma *et al.* [88] developed a U-bent PMMA optical fiber coated with a porous fluorescent polymer that experienced quenching with TNT (LOD: 10 ng/mL) and DNT. Sun *et al.* exploited nanostructure in a polystyrene-pyrene film, creating a fluorescent polymer with self-assembled nanopores to detect DNT vapor [89]. Ma *et al.* observed varied luminescence responses for different nitroaromatic explosives in an organic-inorganic hybrid ultrathin film: quenching for nitrobenzene and dinitrobenzene, an increase in fluorescence from DNT and TNT, and a fluorescence red-shift from picric acid [90]. Li *et al.* exploited the optical properties of an inverse opal photonic crystal, a repeating structure consisting of spherical voids. The photonic crystal was coated with a fluorescent molecule, and was enhanced by the photonic crystal. The fluorescence was quenched with TNT [91]. Li *et al.* developed a sensor array to detect H_2O_2 as an indicator of TATP using CeO_2 nanoparticles. The nanoparticle membranes had a catalytic effect on luminol-H_2O_2 chemiluminescence. The system had a limit of detection of ~30 µg/mL [92].

Much attention has been given to ruthenium compounds, especially tris(bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$, as chemiluminescent materials for use in electrochemiluminescence (ECL)-based explosives detection. The reduction of TATP [93-95], RDX [96], or TNT [97] forms species that react with $Ru(bpy)_3^{2+}$ which generates ECL (see Fig. 4). Ni *et al.* found a limit of detection of 0.7 mg/mL [97] TNT with this method, and Parajuli *et al.* had a limit of ~4 mg/mL TATP [95]. Additionally, Qi *et al.* used ruthenium-doped silicon nanoparticles for TNT detection, through ECL quenching due to resonant energy transfer from excited nanoparticles to a TNT-amine complex [98].

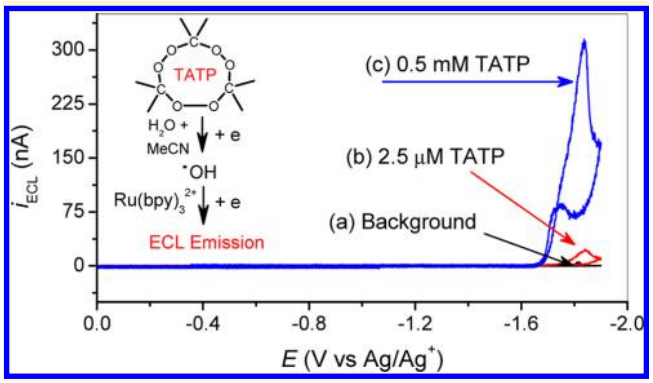

Figure 4: Sensitive detection of TATP using electrogenerated chemiluminescence at a glassy carbon electrode in water-acetonitrile solvent mixture. Reprinted with permission from Ref. 95. © 2010 American Chemical Society

Another process for chemiluminescent-based explosives detection is upconversion luminescence. Ma *et al.* utilized nanocrystals of $NaYF_4$:Yb^{3+}/Er^{3+} coated with amine functional groups to bind to TNT. Upon TNT binding, the fluorescence was quenched. The fluorescence quenching was found to be selective for TNT (LOD: 9.7 ng/mL) over DNT, nitrobenzene, and 2,4,6-trinitrophenol [99]. Tu *et al.* investigated SPR-enhanced upconversion luminescence for TNT; fluorescence increased upon addition of TNT [100].

Raman

Raman spectroscopy is one of the most heavily utilized and actively studied methods of explosive detection due to its powerful identification capabilities and very high selectivity, as has been described in recent reviews [101-103]. The molecular vibrational spectrum that Raman measures has very high information content (large number of sharp spectral features) that is distinct for different molecular structures. These variations in spectra allow the definitive identification of explosives, chemicals, and other nonmetallic materials. Raman scattering is a very inefficient process, with $\sim 10^{-7}$ of incoming photons being inelastically scattered, leaving the molecule vibrationally excited while reducing the energy of the light. Raman measurements require laser excitation, efficient collection of the scattered light, rejection of the excitation light, spectral dispersion, and detection. A number of manufacturers now offer commercially available handheld Raman spectrometers that are portable, easy to use, and come equipped with extensive libraries that can identify unknown chemicals at down to μg quantities based on their spectrum. The largest limitation of Raman identification is the interference from fluorescence.

If the excitation light is resonantly absorbed to produce electronic excitations, either of the sample or of impurities, fluorescence emission with quantum yields often at the level of $>10^{-2}$ can swamp the Raman signal with broadband light that cannot be used for identification. Different Nd:YAG harmonics (266, 355, 532 nm) have been compared for optimizing Raman versus fluorescence signals for explosives detection [104]. Deep ultraviolet (DUV) resonant excitation increases the Raman cross section significantly, and can be performed at such short wavelengths that the interfering fluorescence occurs at wavelengths outside the range of the Raman spectrum [105-109]. DUV excitation is strongly absorbed and thus only probes the surface of materials, so there is a tradeoff between higher cross section of the DUV excitation and the larger number of molecules excited with visible excitation [101]. Since UV light is absorbed in the eye prior to focusing on the retina, UV pulsed lasers have been demonstrated as potential explosive detection platforms operating under eye safe conditions, an important consideration for stand-off measurements [110-112]. Other potential solutions to the fluorescence competition are moving to longer wavelength excitation or using sub-nanosecond time gates [113], since Raman is emitted only during the excitation pulse and fluorescence occurs typically over several nanoseconds. Alternatively, shifted excitation difference methods (taking the difference of two Raman spectra obtained with slightly shifted excitation wavelengths) can be used to remove fluorescence interference [114]. The Raman features shift with excitation wavelength, but the broad fluorescence does not. In the deep UV, Yellampalle *et al.* have adapted a similar scheme with the additional advantage that resonance Raman

features also depend on the wavelength, resulting in dramatic improvements to selectivity and reduction in false positives [115-117].

Performing Raman at stand-off distances is typically performed with nanosecond pulsed laser excitation, collection of signal through a telescope, and gated detection with an intensified CCD camera. These are essentially the same instrumental requirements as LIBS, and both are often employed together[118-121]. Very good signal to noise has been demonstrated for bulk explosive materials (tens of gram quantities) in single shot [122] and multiple pulse [123] spectra measured beyond 100 m in daylight conditions and at 470 m for multiple pulse measurement (1-10 s) during heavy rainfall [124,125].

Raman imaging can be performed in several ways, often combined with stand-off detection. A fiber array can transform the image into a linear stripe along the spectrometer slit, which allows hyperspectral image reconstruction in software [79]. The spectrometer can be replaced with a scanning liquid crystal filter [124,126] or Fabry-Perot interferometer [112] to allow 2-dimensional imaging with spectra acquired over many pulses. Alternatively, point detection can be simply scanned to construct an image [127].

Raman spectra can be measured through opaque and colored plastic containers. Spatially offset Raman spectroscopy (SORS) excites one spot on a sample and looks for multiply scattered photons collected from a spatially offset location. Photons initially from deeper in the sample have a higher probability of multiple scattering and the ratio of signal from deep within the sample to surface excitations increases with spatial offset [128]. Time resolved Raman spectroscopy (TRRS) uses time gating to separate surface scattered photons from those initiated deep within the sample (Fig. 5) [129]. Nitromethane inside an opaque high density polyethylene container was detected at 15 m with SORS and TRRS, showing good separation of signal from the container and the contents [128]. If the containers are at least partially transparent, normal stand-off Raman can be performed without any alterations [121].

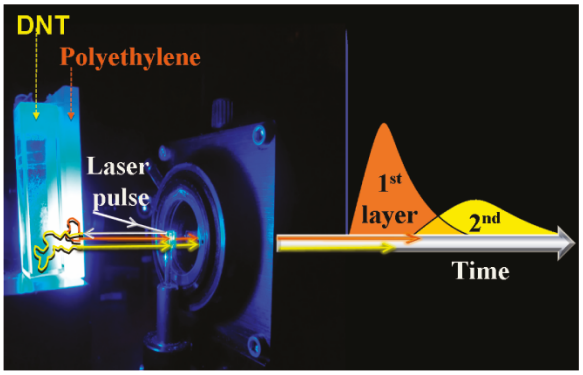

Figure 5. Schematic of the time resolved Raman spectroscopy method using time gating to separate the container wall spectra from the spectra of the material inside, allowing detection of concealed explosives inside containers. Reprinted with permission from Ref. 129. © 2011 American Chemical Society

Coherent Raman

Coherent Raman methods allow excitation of Raman signatures at levels that can be 10^4 times stronger than spontaneous Raman, at the expense of more complicated laser excitation sources [130,131]. Coherent anti-Stokes Raman spectroscopy (CARS) using pulse shaping of a femtosecond supercontinuum was used for spectral identification and scanned

imaging of DNT and other chemicals [132]. Femtosecond CARS with pulse shaping for selective excitation of desired features in explosives has also been demonstrated [133-135]. Femtosecond stimulated Raman scattering using a pulse shaper to achieve spectral resolution (no spectrometer needed) demonstrated raster scanned vibrational imaging for explosive identification to 10 m [136]. Nanosecond CARS has also demonstrated explosive detection and identification [131]. Coherent Raman emits signals only in the forward direction, but for solids, the signal collected is light scattered in the backwards direction. An interesting possibility for detection of gases is optically pumping air so that it lases back at the excitation source, although this has not been made into a practical sensing method yet [137].

SERS

Surface enhanced Raman scattering (SERS) has been widely investigated as a means to exploit Raman spectroscopy for detection and identification of trace explosives [138,103,139] at quantities down to the monolayer level. Details on the SERS method including plasmonic engineering for ultra-trace analysis were reviewed by Baker and Moore [140]. One of the attractions of SERS is the ability to tune the enhancement properties by changing the size and shape of the metal nanostructure. The selectivity of SERS can also be tuned by first adsorbing molecules with different functional groups to the metal surfaces. SERS-active substrates come in many forms. Frequently, they are silver or gold nanoparticles on a dielectric substrate. Additionally, laser ablation of copper [141], silver [142], or gold [143] in solution forms a colloidal, SERS active solution, and has been used to detect ANTA, FOX-7, and TNT.

Recently, much research has focused on the practical aspects of using SERS as an explosives detection method, including using inexpensive COTS products. Several researchers have investigated the use of Klarite™ (Renishaw Diagnostics) as a SERS substrate for explosives detection. Klarite™ consists of a regular array of gold inverted pyramid wells and was shown to be a suitable substrate to detect RDX [144,145], PETN [145,146], and TNT [145-149]. Raza *et al.* [150] developed an alternative inexpensive SERS test strip, consisting of silver nanoparticles grown on filter paper modified with agarose film. The test strips successfully detected TNT.

Like in conventional Raman spectroscopy, the molecular SERS fingerprint can be obscured by contaminants, which is a practical consideration for the use of SERS in an explosives detection device. Researchers have been able to detect 0.15 mg/L RDX in contaminated groundwater using gold nanoparticles [151] and 2 pM TNT in contaminated soil using a complex hybrid microsphere composed of a poly(styrene-*co*-acrylic acid) core and magnetite shell, covered in gold nanospheres and lignin to increase the selectivity of TNT. [152]. Other research in this area has focused on the effect of ions commonly found in groundwater and pH on the efficacy of SERS to detect TNT and NTO [153,154].

The spectral signatures of mixtures of materials can be difficult to separate and successfully identify using SERS. One potential solution is to utilize chromatography to separate components and then perform SERS on the individual constituents, as demonstrated by Zachhuber *et al.* [155], who used microliquid chromatography to separate

two isomers of DNT – 2,4-DNT and 2,6-DNT. Likewise, Talian *et al.* [156] developed silicon-based nanostructured surfaces coated with silver and gold, prepared in a microfluidic channel. They successfully separated and characterized DNB and 2,4-DNT. Jamil *et al.* [143] used a colloidal solution of gold nanoparticles with cysteamine in solution to increase selectivity. The cysteamine and TNT formed a Meisenheimer complex, which was then spontaneously assembled onto the gold nanoparticles and could be detected by SERS. Cysteamine was found to form the complex preferentially with TNT over DNT and picric acid.

SERS can be combined with other technologies to maximize the detection and selectivity for identification of explosives. Buettner *et al.* [148] combined SERS with surface enhanced IR absorption (SEIRA) to differentiate TNT from musk ketone and musk xylene, which have similar chemical structures to TNT but are found in lotions and fragrances. They developed a plasmonic substrate comprised of gold-coated silicon nanopillars that enhances both Raman and IR. Holtoff *et al.* [149] integrated MIPS (molecularly imprinted polymers) with SERS, layering a TNT-imprinted xerogel over gold nanoprisms, however the material was only sensitive to nitroaromatics.

Cavity Ringdown Spectroscopy

Cavity ringdown spectroscopy (CRDS) is a powerful highly sensitive absorption spectroscopy technique for detecting gas phase molecules. In this technique a short laser pulse is injected into a resonant cavity with highly reflective mirrors. As the laser pulse is reflected back and forth between the mirrors the absorbance of the molecules of interest, within the cavity, is determined by the exponential decay of the intensity of the light over time. In many cases, this method utilizes an optical path length many times the sample path length and measurement of the material concentration is immune to laser pulse intensity fluxuations. Spicer, Wojtas and Caygill have recently written reviews, which cover CRDS [157-159].

Many conventional explosives have very low vapor pressure making atmospheric room temperature CRDS measurements of explosives challenging. Fortunately NO_2 gas has a strong absorption in the UV from 400-450 nm and NO and N_2O absorb in the IR (5.26 μm and 4.55 μm respectively). Gas concentrators [158] and catalytic reactions with platinum (IV) oxide hydrate [160] have been used to detect NO_2 to the ppbv level. Specifically, catalytic thermal dissociation using platinum oxide hydrate on TNT, 2,4-DNT, and 1,3-DNB to produce NO_2 was detected at the 0.5 ppbv level using UV-CRDS without sample preconcentration after only one second of data acquisition [160]. Wojtas showed practical application of the preconcentration technique through detection of NO_2 at a limit of 10-100 ppbv from AN and NG in a Polish mine facility [161].

In 2010 Snels revealed that IR-CRDS (1.6-1.7 μm) did not have the sensitivity to detect explosive vapors at room temperature but they successfully detected 75 ng of solid DNT and TNT when flash heated within the optical cavity [162]. Such detection limits potentially allow detection of fingerprint amounts of explosives (0.1 μg-1 mg in the first generation print) with CRDS [162]. A free flowing liquid wire jet soap film containing picric

acid placed within the ringdown cavity at the Brewster's angle allowed for detection of <17 fmol of picric acid when using a 355 nm UV-CRDS system [163].

Notable advancements have been recently made by Harb *et al.* [73,164]. In 2012 they utilized extended Kalman filter methods or real-time data processing using a frequency domain analysis technique, instead of the typical Levenberg-Marquardt method, to obtain real time detection of the vapor from a small piece of solid TNT in a CRDS cell [164]. The real-time absorption measurements were obtained while rapidly (0.2-7 s) scanning the infrared quantum cascade laser (QCL) from 1580-1700cm^{-1}. More recently pulsed quantum cascade systems operating between 1200-1320 and 1316-1613 cm^{-1} were used to measure headspace gases at ppm levels of NM and NG in less than four seconds. During the four seconds >150,000 spectral data points were obtained and analyzed using the frequency domain analysis approach while scanning the QCL. This novel analysis technique allowed for atmospheric pressure and temperature measurements of NM at the ppbv level. Headspace measurements of acetone, a possible TATP impurity, were made with the sample up to a few meters away from the CRD cell input port. Future work will allow for more than two lasers to be resonant in the cavity simultaneously allowing for a very large spectral bandwidth to be covered in a small amount of time [73].

Laser Induced Breakdown Spectroscopy

To date, most laser induced breakdown spectroscopy (LIBS) work has been performed on conventional explosives from trace (fingerprints – μg to mg quantities) to bulk (gram) quantities [165]. Intense short duration (femtosecond (fs) to nanosecond (ns)) laser pulses at stand-off or near field distances are utilized to ablate a sample and sometimes substrate, to generate an evolving plasma. Emission from a mixture of molecules, atoms, and ions in various rapidly evolving excited states is collected and chemometrics/analysis of the C, H, O, N, Cl, CN components is performed. Reviews within the past five years highlight the different techniques [166-169,165,101,170]. Recent work has shown the effects of substrate and interferent dependence [171] on analyte classification and how selective sampling can enable surface sensitivity [172-176]. Effects due to wind [177], thermal radiation [166,178,179], and different atmospheres [179-181] were also investigated.

Signal enhancement through dual pulse LIBS increased analyte signal by up to an order of magnitude, but was found to be dependent on a the substrate and element investigated [165]. Using a CO_2 laser as the second pulse efficiently reheats the plasma plume through an inverse Bremsstrahlung absorption process without increasing the quantity of ablated mass [166,182]. More recently a geometry dependent, single beam splitting LIBS approach exhibited signal enhancement (~5x) due to the angle and energy of the second beam and not the timing [183]. Remote filamentation induced breakdown spectroscopy (R-FIBS) uses ultrashort fs lasers to induce a filament in the atmosphere over distances up to a kilometer with no need for focusing optics [168]. In general, the ultrashort timescale of fs-LIBS allows for ablation of the sample material before energy has time to transfer into the substrate, allowing for detection of smaller amounts of material. Elemental emission is fluence dependent so more energy results in more signal [184] and the lower temperature plasmas observed in fs-LIBS result in less fragmentation of the explosive molecules and subsequently larger molecular fragment emissions [185]. Time resolved fs-LIBS experiments on RDX, TNT and NTO under different atmospheres show CN

emission is from a secondary reaction from the surrounding nitrogen environment within 150 ns [181].

Some improvised explosives and their precursors have been investigated using LIBS excited at 1064 nm [186]. A significant advance to observe molecular fragment emissions in the mid-wave IR and long-wave IR from 4-12 μm was achieved by Yang *et al*. [187] High energy (>10 mJ) fs-LIBS (<750 fs) allowed for preservation of the 420 nm NO_x signature from KNO_2 and $NaNO_3$ [185]. Weathering effects on chloratite (mixture of $NaClO_3$, $KClO_3$, sulfur, and sugar) fingerprints (Fig. 6) showed that a good signal was obtainable for only two weeks [173].

Much effort has been made in the chemometrics/analysis of LIBS emission spectra to enhance classification models and decrease the number of false positives [188,189]. Linear analysis was found to be insufficient necessitating multivariate analysis [190]. Partial least squares discriminate analysis [175,178,191] and machine learning classifiers with supervised learning methods [189,172,192] are two of the more common techniques. Combining LIBS with Raman spectroscopy has increased the ability to identify unknown materials at stand-off distances through sensor/data fusion (Fig. 7 shows an example) [193,119,194-196]. As high -energy lasers become more portable LIBS fieldability is improving [197,184,168]. Hand held near field low power (<1 mW) 1064 nm LIBS devices are currently commercially available for metal analysis, indicating applications to explosives detection are not far behind [198,199].

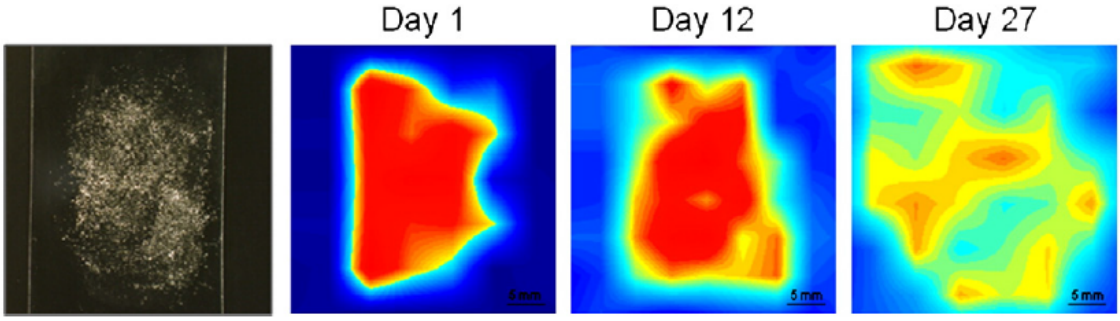

Figure 6. Linear LIBS scanning of weathered chloratite fingerprints on Al surface at 31 m stand-off. Emission from Na line at 589.2 nm shown as a function of increasing age after deposition. Reprinted with permission from Ref. 173. © 2013 Elsevier

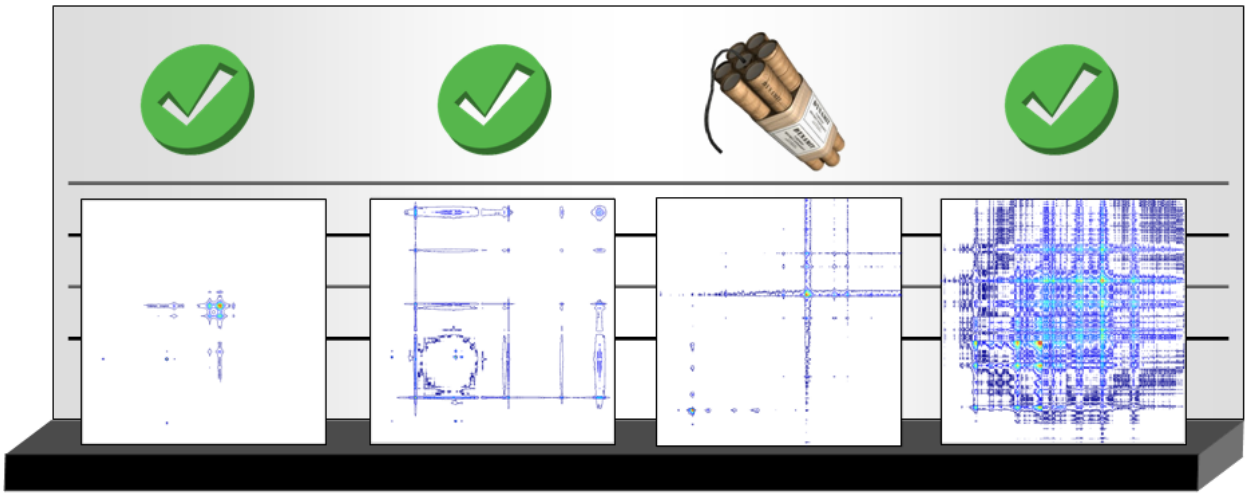

Figure 7: Illustration of Raman – LIBS spectral output fusion. The process uses a mathematical treatment to produce a two dimension image of target analytes and matrix / interference materials by assembling the Raman and LIBS spectra and using simple correlation coefficient values from the 2D images and those achieved using Raman and LIBS spectra separately. Reprinted with permission from Ref. 195. © 2011 American Chemical Society

Photoacoustic Spectroscopy

In typical laser photoacoustic spectroscopy (PAS), alternating electromagnetic radiation (pulsed/chopped) is absorbed by a sample and converted into heat by a non-radiative de-excitation process. Ambient air absorbs the heat and the rapid sample heating/cooling due to the alternating chopped/pulsed light causes a pressure fluctuation or photoacoustic wave that can be monitored using a microphone or laser vibrometer [200]. Use of a cavity cell containing a gas or solid material and enhanced microphones have shown better than parts-per-billion by volume (ppbv) detection sensitivity for trace gas analysis of non-explosives [201]. To enhance the photoacoustic signal to a part per trillion (pptv) detection level, piezoelectric transducers [202,203], as simple as a quartz resonator in the form of a tuning fork, can be used and the method is called quartz enhanced laser photoacoustic spectroscopy (QE-PAS) [203]. PAS signal strength is proportional to laser pulse energy. In stand-off PAS, as the acoustic wave propagates, the pressure amplitude signal strength decays with a 1/r dependence [202].

Photoacoustic spectroscopy is selective (characteristic rotational and vibrational absorption), sensitive (~1 ng TNT [204]) and can be used without sample preparation. It is also advantageous because it is not sensitive to light scattering due to the substrate but only absorption of optical radiation [204]. Alternatively, care must be taken to ensure there are not interferences with other substances such as atmospheric gases [205], other explosives, and background noise [206]. Ideally the background/sample surface should be transparent to the affects of the excitation laser, but in practical application this is problematic. The sensitivity or selectivity of PAS can be enhanced by combining it with other detection techniques such as resonant microcantilevers or UV spectroscopy. The works of Dongkyu and Van Neste are good examples of combined techniques [207,208]. A portable off-the-self PAS device utilizes UV light to vaporize and dissociate materials such as explosives which then emit ultrasonic photoacoustic signals [209].

Recent advancements with quantum cascade lasers (QCL) have led to enhanced photoacoustic techniques whereby the sample surface is exposed to tunable laser radiation within the materials characteristic absorption band. As the laser wavelength is scanned the photoacoustic response is measured using a microphone or QE-PAS and photoacoustic spectra corresponding to the rotational-vibrational energy absorption specific to the chemical species are obtained. In 2010, QE-PAS was successfully used in a 20 m stand-off configuration with a 100 mW QCL (9.25-9.80 μm) to detect RDX at a surface concentration of ~100ng/cm^2 [210]. Work of Sharma *et al.* showed stand-off distance was dependent on the background substrate material. DNT and PETN on diffused Al, scanned over 1160-1400 cm^{-1} and 880-915cm^{-1}, showed a 5 μg/cm^2 sensitivity with 12 m range, while a wood surface required 50 μg/cm^2 to yield only a 6 m range [211]. Short stand-off detection (8 inches) of bulk TNT (1 mg/mm^2) was obtained utilizing a ultrasensitive microphone and increased to 2.5 m using a 0.6 m diameter parabolic sound reflector [202,206]. The C-O stretch, centered near 8.3 μm, of the homemade explosive TATP was detected in the gas phase in the near field using QE-PAS [205,212]. Multivariate analysis has also been used in combination with IR (9-11μm, 30-500mW) scanning PAS in a cavity cell configuration to identify less than 100 μg of DNT, TNT, Tetryl, RDX, HMX, PETN and TATP [213].

Outlook

The expanding number, quality, and breadth of explosives detection methodologies are encouraging the development of ever more capable instruments, for both laboratory and field use. Instrumentation for X-ray diffraction methods is being rapidly advanced, so that the identification advantages of X-ray diffraction over X-ray imaging can be realized in screening applications. Terahertz imaging with spectral resolution appears to be on the brink of application to enhanced personnel screening applications with the ability to identify contraband materials, although issues related to spectral feature modification due to texture or covering materials must still be resolved. Both active and passive infrared spectral imaging methods are improving their detection limits as well as their identification abilities. However, methods must improve their abilities in backscattering or emission geometries, which can cause peaks to look absorptive, dispersive, or intermediate between the two due to particle size, shape and environment. We look forward to significant developments where chemiluminescence technologies are embodied into swipe or glove type sampling methods to analyze suspect areas or investigate individuals or objects in close to real time. Although Raman appears to be one of the most mature explosives detection methods, significant improvements are still possible including new hardware for Raman imaging, further reduction in fluorescence interference as in SORS or TRRS via novel laser sources, wavelength modulation, or new detectors, combinations of Raman with other technologies (beyond ATR-FTIR or LIBS which are currently actively pursued). Similarly, hybridization of methods, such as SERS with SEIRA or MIPS, as well as advances in data fusion computational tools, will lead to improved ROC curves and areas of application. Large area screening for trace gases indicative of contraband materials is quickly becoming realized especially using new cavity ringdown spectroscopic methods and other long-path absorption tools. Data fusion methods are improving the probability of detection and identification from ever-smaller samples and ever more complicated explosive materials, including the increasingly prevalent homemade explosives.

Nevertheless, methods to fuse data or information from more disparate and larger numbers of methods to achieve greater certainty of detection or increased discrimination between threat and non-threat are needed.

Explosives Glossary

AN – ammonium nitrate
ANTA - 3-amino-5-nitro-1,2,4-triazole
DNB – dinitrobenzene (isomers 1,3-DNB and 1,4-DNB)
DNT – dinitrotoluene (isomers 2,4-DNT and 2,6-DNT)
FOX-7 – 1,1-diamino-2,2-dinitroethene (DADNE)
HME – homemade explosive
HMTD – hexamethylene triperoxide diamine
HMX – octagen; octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
IED – improvised explosive device
Picric acid - 2,4,6-trinitrophenol
NG - nitroglycerine; nitro; glyceryl trinitrate; RNG; trinitroglycerine
NTO - nitrotriazalone
PETN – pentaerythrytol tetranitrate; 2,2-bis[(nitroxy)methyl]-1,3-propanediol, dinitrate
RDX - cyclonite; hexogen; hexahydro-1,3,5-trinitro-1,3,5-triazine
Semtex - composition of PETN (or RDX and PETN) with heavy oils and rubbers
TATP – triacetone triperoxide
Tetryl - methyl-2,4,6-trinitrophenylnitramine
TNT - 2,4,6-trinitrotoluene; 2-methyl-1,3,5-trinitro-benzene

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