

Night Vision and Electronic Sensors Directorate

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Investigations of Novel Sensor Technology for Explosive Specific Detection

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Fort Belvoir, Virginia 22060-5806

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By

Aaron Lapointe

December 2009

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**Science and Technology Division
FORT BELVOIR, VIRGINIA 22060-5806**

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Investigations of novel sensor technology for explosive specific detection from a military perspective

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by

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1.0 Acronyms

ACTC	arylene-ethynylene tetracycle
AFP	Amplifying fluorescent polymers
CARS	Coherent anti-stokes spectroscopy
CD	Cyclodextrin
CNT	Carbon nanotubes
COTS	Commercial-off-the-shelf
CWA	Chemical warfare agents
DHS	Department of Homeland Security
DMMP	Dimethylmethylphosphate
DNB	Dinitrobenzene
DNT	2,4- or 2,6-, or 4,6- dinitrotoluene
DoD	Department of Defense
DRS	Differential reflectometry spectroscopy
EPA	Environmental Protection Agency
ERCs	Explosive related compounds
FCS	Future Combat Systems
FP	Fabry-Perot
GC	Gas Chromatography
HMX	Octahydro 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane
HT-IMS	Hadamard transform – ion mobility spectrometry
IED	Improvised explosive device
IMS	Ion mobility spectrometry
IR	Infrared
ITMS	Ion trap mass spectrometry
LDA	Linear discriminant analysis
LIBS	Laser induced breakdown spectroscopy
LIF	Laser induced fluorescence
LOD	Limit of detection
MIPs	Molecularly imprinted polymers
MS	Mass spectrometry
MWNT	Multi-walled carbon nanotubes
NG	Nitroglycerin
NRL	Naval Research Laboratory
NVESD	Night Vision and Electronic Sensors Directorate
OFRR	Optofluidic ring resonator
OTFT	Organic thin film transistors
PDS	Photothermal deflection spectroscopy
PETN	Pentaerythritol Tetranitrate
PF-LIF	Photo-fragmentation-laser induced fluorescence
Ppb	Parts per billion
Ppm	Parts per million
Ppt	Parts per trillion
PSi MC	Porous silicon microcavity

RDX	Hexahydro 1,3,5-trinitroperhydro-1,3,5-triazine
RS	Raman spectroscopy
SAMs	Self assembled monolayers
SAW	Surface acoustic wave
SERRS	Surface enhanced resonance Raman spectroscopy
SNB	Signal-to-background
SNR	Signal-to-noise ratio
SWAP	Size, weight, and power
SWNT	Single-walled carbon nanotubes
THz-TDS	Terahertz – time domain spectroscopy
TNB	1,3,5-Trinitrobenzene
TNT	2,4,6-Trinitrotoluene
TSA	Transportation Security Administration
UV	Ultraviolet
VOCs	Volatile organic compounds

2.0 Project Summary

The objective of this challenge project was to investigate explosive specific sensor technology to fill capability gaps for the U.S. warfighter. Inquiries into current sensor systems were made and may provide near term solutions while investigation of nascent and evolving sensor technology presented potential long term solutions with enhanced capability. This project is inspired by the need to develop sensors that detect the presence of explosive specific threats across a wide range of military applications, which include extreme conditions and complex urban environments.

Previous work has assessed potentially successful explosive sensor technologies, though they have focused on homeland security applications. For example, Moore's [1] work provided an assessment of current laboratory analytical methods and summarized recent publications without discussing the impact of real-world environments. In addition, National Research Council's [2] report included a discussion of standoff detection candidates although military applications were not incorporated. This project will attempt to account for specific end-user scenarios, future platforms, and environmental conditions that directly affect assessing sensor candidates.

Recent advances in sensor technology have demonstrated the capability to identify vapor phase explosive species in close proximity (less than one meter), and in real-time. These advances have lead to further research and development to improve the state-of-the-art. Since enemy combatants are continuing to deploy more complex IED-like threats, there is a strong push to provide a *standoff* capability to detect explosive threats at increased distances in order increase survivability. Standoff is most widely defined as the distance between the sensing system and the target of interest. In addition, capability for *remote* deployment of sensor technology on robotic platform or articulating arm is also strongly encouraged as the Army's Future Combat Systems (FCS) continues to evolve. Distinctly different from standoff, the ability to integrate sensor technology onto a mobile platform and sample a target, or area of interest, in close proximity while controlling from a distance is defined as remote.

Within the following report, three specific topic areas were investigated, sensor platforms, novel sensory materials, and standoff sensing techniques. Sensor platforms and sensory materials addressed the remote applications while standoff sensing techniques addressed standoff applications. This report is not intended to cover all existing or novel sensor technologies that attempt to sense the presence of explosive threats.

The categories below list sensor technologies that reflect potential near-, mid-, and far-term maturity for deployment in military applications. Since these evaluations are based on the published information, not all papers discuss maturity-related criterion nor do they address all evaluation criterion described in later sections of this paper. Since these technologies are all still in the development phase and experiments are completed under different conditions, direct quantitative analysis is limited. Given these constraints, the

sensor technologies described in this paper (sensor platform, sensory materials, and standoff sensing) are compiled below.

Sensor platforms

<i>Near</i>	<i>Mid</i>	<i>Far</i>
IMS	Integrated IM-MS	CNTs
ITMS	Microcantilevers	Lab-on-a-chip devices
SAW devices	OTFTs	Microfluidic sampling
Micro-preconcentrator	HT-IMS	Micro-ring Resonators
Subsurface IMS	FP sensor	Nanofibrous membranes
	SERS/SERRS	Self-powered sensors
		PSi microcavities

Sensory Materials

<i>Near</i>	<i>Mid</i>	<i>Far</i>
Penttiptycenes	Turn-on Fluorescence	Biomimetic coatings
Photoluminescent part.	Pyrene quenching assay	Pyrrole receptors
		Fluorescent nanofibril
		Cyclodextrin MIPs

Standoff Sensing

<i>Near</i>	<i>Mid</i>	<i>Far</i>
LIBS	PDS	CARS
PF-LIF	DRS	THz-TDS
	Resonance Raman	

The following paper details many technologies that support the following conclusions. For sensor platforms, SAW devices and enhancements to IMS offer potential near term solutions due to robustness and are COTS systems that can be modified for military applications. For mid and far-term solutions, microcantilevers and CNTs may hold the best overall potential due to their extremely efficient transduction mechanisms ensuring low detection limits. For sensory materials, combining those described into a sensor array could provide an effective sensing solution. Fluorescing polymers and biomimetic coatings are believed to potentially offer the most selective and versatile material that could be tailored to many target analytes. Investigation of standoff sensing methods produced a wide variety of technologies that have recently received much attention due to current IED problems in OIF and OEF. LIBS and Resonance Raman sensing methods demonstrated good overall attributes for military applications due to the ability to detect the full range of ERCs and can expand their libraries for new target analytes.

3.0 Introduction

Current commercial-off-the-shelf (COTS) explosive specific sensors are designed to meet the current market needs of the Department of Homeland Security (DHS) and Transportation Security Administration (TSA). The applications include airport and train depot screening, port and cargo screening, and certain public landmarks, such as Ellis Island, New York, among others. Naturally, these environments are much different than those presented to US warfighter in Iraq and Afghanistan. Working in the explosive sensor development community over the past few years, it is clear that there is a major disconnect between technology solutions deployed for current domestic civilian applications versus the need of the military. In addition, very little ‘real world’ test data is available to properly assess new and existing sensor systems against the military application. The purpose of this project is to acquire a better understanding of sensor candidates for the Army’s potential future investment. Clearly stated, the level of research and development funding would not be available if there was an existing sensing capability that met the warfighter’s need.

Since the Vietnam War, and other large- and small-scale incidents leading to the present, it is clear the use of explosives to attack targets *covertly* will continue into the future. Previous conventional wisdom and military doctrine regarding battlefield tactics do not apply to the current theater of asymmetric warfare occurring in Operation Iraqi Freedom (OIF) and Operation Enduring Freedom (OEF) in Afghanistan. In recent years, the use of improvised explosive devices (IEDs) throughout the world has been the primary weapon of terrorist groups. A more detailed description of IEDs will be provided. As terrorist’s tactics lead to countermeasures, new counter tactics emerge. There are many existing defensive layers, including fortified bases, increased security patrol and intelligence, which must work in concert to defend against explosive threats. Other technological tools are emerging to join the fight in the war on terror. One specific means to combating the success rate of these covert explosive threats is to develop technological capabilities to detect them in advance of their intended use. It is envisioned that these technology solutions will directly improve the toolset of the user in order to make a more informed decision, and consequently save lives.

In order to provide hi-tech solutions and sensor systems for field deployment, one must properly assess the technology candidates. There has been much debate over recent years regarding potential technological solutions to explosive detection for military applications. Due to the complex nature of the operation environment and multiple applications, it is quite clear that no one technology will provide across the board detection capability. In addition, most mature sensors that detect explosives have simply not been designed for military applications. This reality presents many unknowns for potential sensor system candidates. Decisions regarding future research and development need thorough vetting of key figures of merit. The motivation of this project was driven by the need to provide the Army with the knowledge to develop an explosive threat sensing capability for near and long term planning.

4.0 Objectives

This challenge project proposes to complete multiple objectives.

- First, investigate COTS explosive specific sensors to determine their applicability to current military threats. This objective examines any potential near-term solutions.
- Second, investigate novel sensing technologies that have demonstrated proof of principle and are believed to provide extended capability given further investment. Proof of principle incorporates those technologies that have experimented with explosives of interest at concentration levels near equilibrium vapor pressure. This objective will require investigation of current basic and applied research investments and evaluate technologies as potential mid-, and far-term solutions. There may be limited published information for some technologies, although efforts will be made to include those technologies that have at least provided proof of principle.
- Third, recommendations from the first two objectives will list the most likely near-, mid-, and far-term sensor candidates and investment opportunities.
- Lastly, a capability matrix of sensor solutions and their expected measure against evaluation criterion will be constructed.

5.0 Description of the IED Problem

The experiences of the last few years confirm that IEDs will be an omnipresent future threat to our troops. Detection of IEDs is complicated by many factors including device variation, device concealment, triggering mechanism, environment, among others. Chemical signatures are not constant and depend heavily on environmental conditions and duration of emplacement. Insurgent countermeasure innovations in response to defeat technologies have demonstrated that it is important to develop detection schemes that are device independent. As a result most have come to the conclusion that the most robust detection schemes should not focus on the devices, but should be explosive specific.

The IED threat can be dissected into different deployment scenarios including roadside IEDs, vehicle-borne IEDs (VBIED), and human-borne IEDs (HBIED). Current programs are focused on these IED threats in addition to bomb making facilities and weapon caches. Naturally, there are security concerns when describing in detail how these IEDs have been deployed. This project focuses solely on information approved for public release. Over the last few decades, chemical explosive signature research (at Sandia National Laboratory, Cold Regions Research Laboratory, etc.) has been performed on fate and transport of landmine related chemicals in soils although it is not directly applicable to the IED threat. In addition, there is limited information regarding background and IED chemical signatures in Iraq and Afghanistan. Roadside IEDs have been found in many different concealment scenarios. Concealment of roadside IEDs

creates a different chemical environment that may alter a sensor's response. In most cases, the roadside scenario places the explosive device directly in the atmospheric environment which may alter residue and vapor signature due to solar loading and wind effects, respectively.

Deployment of VBIEDs creates a different chemical signature with factors that differ from roadside IEDs. Typically, larger amounts of explosives are used in VBIEDs with most likely a similar level of concealment. Explosives housed within an enclosed volume may create larger vapor signatures through window cracks and door seals. Exterior residues on vehicles may behave similar to those of roadside IEDs. Acquiring spectral signatures for bulk detection technologies may be difficult due to lack of vehicle exterior penetration, although some techniques have demonstrated success. HBIEDs, or suicide bombers, consist of people that may have come into contact with explosives. Additional applications have been created that entail sampling suspects to investigate potential for terrorist involvement. The chemical signature of an HBIED will have additional chemical signatures compared to roadside or VBIEDs due to additional oils and substances that exist on hands and clothing. This target may have a much higher background signal possibly contributing to higher false alarms although HBIED detection can provide an important application of explosive sensing.

Bomb making facilities and weapon caches, as shown in Figure 1, are additional threat scenarios. Higher explosive related compound (ERC) signatures are expected surrounding these target types, although higher background signatures may also be present. Detecting these targets may require both standoff and remote capabilities. Bulk detection is likely to be more successful detecting weapon caches while trace detection may be more applicable to bomb making facilities.



Figure 1: Picture of a weapons cache discovered with multiple artillery shells.

5.1 Relevance to Army/NVESD

Improving survivability and situational awareness of U.S soldiers is the primary goal of most sensor research and development programs. Develop, test, integrate and transition sensors that detect landmines and IEDs is the objective of current funded programs within Night Vision and Electronic Sensors Directorate (NVESD), the sponsoring organization of this challenge project. This project is responsible for investigation, development, testing, and maturation of technologies capable of providing chemical identification of explosive species at standoff distances. By increasing the detection

distance, a standoff sensing capability, would provide improved survivability of the end user from the IED blast radius, which is illustrated below in Figure 2. As one may expect, additional technologies, not addressed in the SED ATO, will need to be assessed to evaluate potential capability.

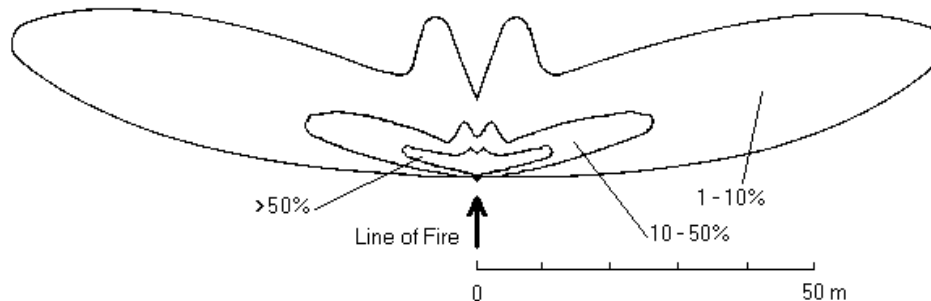


Figure 2: Percentage of Casualties standing around an 87.5 mm artillery shell. [9]

In summary, there are multiple reasons discussed above that demonstrate the relevance of this challenge project to NVESD. The past, present, and future research thrusts focus on countermine and counter-IED solutions. Funded programs currently exist to investigate standoff explosive sensor development. The core competency of investigating explosive sensing capabilities, developing and testing sensor systems, and finally transitioning sensors to systems research or direct customers has been demonstrated. In addition, there are established partnerships between NVESD and other parts of the development chain from universities to end user organizations. This challenge project aims to improve the knowledge base of NVESD and strengthen future paths for research and development.

5.2 Explosive Types of Interest

TNT	2,4,6 – Trinitrotoluene
DNT	2,4 or 2,6 – Dinitrotoluene
RDX	Hexahydro 1,3,5-trinitroperhydro-1,3,5-triazine
PETN	Pentaerythritol Tetranitrate
HMX	Octahydro 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane
AN	Ammonium Nitrate
ANFO	Ammonium Nitrate with Fuel oil
UN	Urea Nitrate
NG	Nitroglycerin

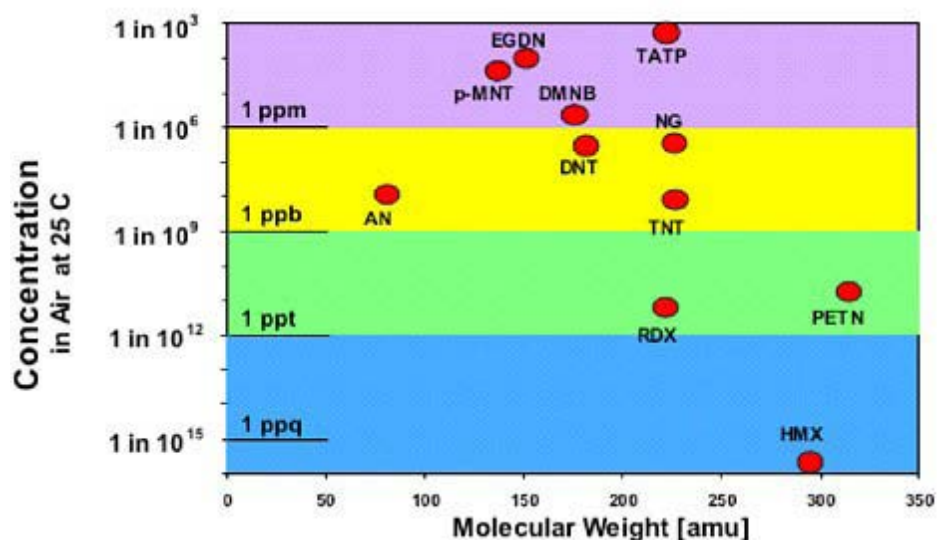


Figure 3: Vapor pressures of common explosives.
Courtesy of J. Parmeter et al., Sandia National Laboratory.

5.3 Key Evaluation Criteria

Explosive specific chemical sensing can be separated in two major groups, *trace* and *bulk* detection. Bulk detection typically involves imaging of the target while identifying the explosive embedded within a concealed device. Bulk sensing technologies are designed to detect key features that involve properties of constitutive atomic elements, since they operate at high excitation energies with high penetration potential. Typically, relatively large amounts of explosive material are needed to respond effectively within its dynamic range. Trace detection methods respond to vapors, airborne particulates, and surface residues surrounding the explosive device of interest. These methods typically deliver atomic, ionic, fragment, parent molecule, and molecular cluster information. Since trace detection directly interacts with the surrounding environment, there are many sources of false alarms with high background signals, punishing selectivity. Many new research initiatives are striving to combine both methods to create a more comprehensive orthogonal solution.

In order for one to evaluate sensor technologies across the spectrum of maturity, performance criteria need to be identified. These criteria take into account the most important aspects and constraints of the user's needs. Other criterion will be accounted for such as, size, weight, and power (SWAP), which are critical to future integration with Army FCS platforms and vehicles. Other factors such as cost and fieldability are more difficult to account for with regards to emerging and nascent technologies. Most importantly, the respective weights of these criteria differ between DHS and DoD applications. Naturally, the perspective of the DoD is focus of this project.

Selectivity: The ability of sensor technology to discriminate between the target of interest and background noise. Also, discrimination between explosive compounds within the same family (i.e. nitroaromatics) is also important. This may prove difficult for most

trace detection methods due to interaction with surrounding environment that may consist of molecules made from the same elements that make up most conventional high explosives (carbon, hydrogen, oxygen and nitrogen) although in different ratios.

Sensitivity: This criterion addresses the change in unit sensor response with the change in unit target analyte concentration. It is also defined by the slope in the calibration curve.

Limit of Detection (LOD): This criterion identifies the lowest amount of material needed to create a sensor response that is greater than a signal-to-noise ratio (SNR) or signal-to-background (SNB) or three. It is important to distinguish that only a reliable signal within the sensing dynamic range qualifies as a limit of detection.

Response Time: The amount of time needed to begin sampling the target space, acquire signal from target, process the signal, and display the response to the user defines the time needed for one response. This criterion is very critical from a military perspective, due to the need for real-time responses.

Range of substances: A list of explosive types that can be detected by one sensor is important for many DoD applications. Due to a variety of sensing mechanisms, some technologies may be able to respond to more ERCs than others. As terrorist groups become more sophisticated, this criterion becomes more important.

Detection Distance: This criterion will differ widely for all sensing methods to be evaluated, although it is more specifically focused on standoff sensing technologies. The value will define the distance between the sensor and target of interest.

Recovery/Reversibility: This criterion defines the ability of the sensor to recover to its baseline response after exposure to an explosive sample. This criterion is most relevant to sensory materials where physical samples of the target analyte come in contact with sensor substrate. This has great impact for practical real world applications. Without reversibility, cost and logistics of consumables may override other advantages.

Dynamic Range: Defines the reliability of sensor response between the sensor's LOD to the maximum concentration detectable maintaining a linear progression.

6.0 Technology Investigations

The following investigations focus on COTS and novel sensing technologies that detect the specific explosive chemical signature, including both bulk and trace methodologies. As described in earlier sections, successful development and deployment of these technologies will include encountering urban scenarios and complex environments that may create very high background signals for techniques that rely solely on the signature of the explosive device, or bulk detection. In addition, urban and complex environments will also present problems for trace detection due to a wide array of chemicals that may cause false alarms. With the wide array of technologies to investigate, focus was given strictly to those techniques that could potentially deliver more capability to the

warfighter. In addition, there was a balance between the depth of investigation for each technology and the breadth of including more and more applicable techniques. Integration onto the Army's FCS platforms and vehicles will drive the discussion on potential methods that inherently decrease size, weight, and power (SWAP). In order for future solutions to be viable, decisions to down-select technology development simply needs to occur.

6.1 COTS State-of-the-Art – Bulk Detection Methods

There have been few field deployed bulk detection systems. For example, X-Ray Backscatter imaging, or Z Backscatter developed by American Science & Engineering, provides the capability to identify high dense regions of low atomic number. Transmission imaging of X-rays detects objects with greater density because they block or absorb more X-rays than objects with less density. By comparison, a Z Backscatter image captures data from X-ray photons that are scattered from the object undergoing excitation. X-ray photons scatter differently when they encounter different types of materials, known as Compton Scattering. This process is material-dependent, with the lower atomic number materials scattering stronger than higher numbered ones. [10] While these advances have demonstrated imaging improvements, this method is not specific to explosive compounds, which may cause high probability of false alarms. Other bulk detection methods such as millimeter wave imaging, Computed Tomography (CT), X-ray diffraction (XRD), and neutron gamma may not be directly applicable to the military applications described earlier regarding IEDs and bomb making facilities. The following descriptions identify techniques that either have been fielded or are potential enhancements from recent publications.

6.1.1 Nuclear Quadrupole Resonance (NQR). NQR has been developed for limited applications including detection of plastic landmines, due to their lack of metal content. It operates similarly to Nuclear Magnetic Resonance (NMR), although no external magnetic field is required. NQR utilizes an electron cloud to split the nuclear spin states through electrostatic interaction with the nuclear charge density. When the nuclei have quantum spin states higher than 1, such as ^{14}N , than it can be targeted. [12] This technique offers very specific information about the chemical structure, which results in high selectivity. Drawbacks from the field include long dwell times needed over buried targets in order to acquire enough signal and bulky, high-power consuming equipment.

6.1.2 High Temperature Superconductor (HTS) for NQR. As mentioned above NQR has long held promise for the detection of explosives, however, poor sensitivity has lead to long measurement times and high false alarm rates. One path to improve the sensitivity is to improve the SNR of the detector. The SNR of a magnetic resonance sensor goes roughly as the square root of the Q-value ($f_0/4f$). Much of the previous work in NQR has relied on coils of normal metal, limiting Q-values to less than 500. Recently, Wilker et al [58] explored using high temperature superconductor (HTS) sensors with Q-values greater than 5,000. HTS materials have losses hundreds to thousands of times smaller than copper. They observed that at the lowest pulse power applied, the measured Q-value was greater than 400,000. [58] While field deployment of NQR may not

currently be practical, due to the need for cryogenic cooling, advancements such as HTS sensors may enhance SNR enough to explore further development, assuming HTS sensors can be easily fielded.

6.1.3 RF atomic magnetometer for NQR. Savukov et al [56] have demonstrated the first detection of proton NMR signals with an rf atomic magnetometer. The advantages of this technique include relative insensitivity to ambient magnetic field noise as well as the possibility of measuring NMR chemical shifts. Comparing it with that of an atomic magnetometer they found that atomic magnetometers have an intrinsic sensitivity advantage over a pick-up coil for frequencies below about 50 MHz, thus, they are well-suited for detection of NQR signals. [56] In addition to HTS sensors, there have been other concepts that improve upon the sensitivity of conventional pickup coil detection by using superconducting resonators and sensors operating at cryogenic temperatures. Lee et al [57] demonstrated the first detection of NQR with an atomic magnetometer and showed that a cryogen-free atomic magnetometer, with intrinsically frequency-independent sensitivity and easy tuning/damping capabilities, could make an attractive new tool for detecting magnetic resonance signals in the kilohertz to megahertz range. They concluded that the demonstrated sensitivity of the atomic magnetometer is significantly higher than that of a pickup coil probe, for samples that have to be placed outside the volume of the coil. In addition, an atomic magnetometer is much less susceptible to electronic interference because the detected NQR signal is on the order of a microvolt, whereas a typical NQR signal from a pickup coil is in the nanovolt range. [57] Since this work was completed in a laboratory environment, the same enhancement in would need to be realized in a more open environment, where external rf noise is canceled by subtracting signals from more than one probe beam. If this enhancement can be successfully tested, it could potentially lead to a mobile atomic NQR spectrometer for various field applications. [57]

6.2 COTS State-of-the-Art – Trace Detection Methods

The following technology descriptions include trace detection technologies that depend on small amount of the target material. In some cases, a physical sample is needed to be processed for analysis, while other methods use optical means to excite and collect emitted photons from the target compounds.

6.2.1 Ion Mobility Spectrometry (IMS). IMS identifies compounds based on the amount of time it takes for ionized molecules to pass through an electrified field in a tube. This time, sometimes called “time of flight” or “drift time”, is then compared to a database containing the transit times of previous analyzed compounds, making it possible to distinguish the target material from other molecules. Common problems observed involve the use of pure chemicals used to calibrate the drift time while attempting to detect military grade explosives that include non-pure materials with other substances such as binders, plasticizers and solvents. Not calibrating with real-world materials may increase the probability of false alarms. In addition, these systems suffer from inability to clear after heavy exposure of explosive contaminants.

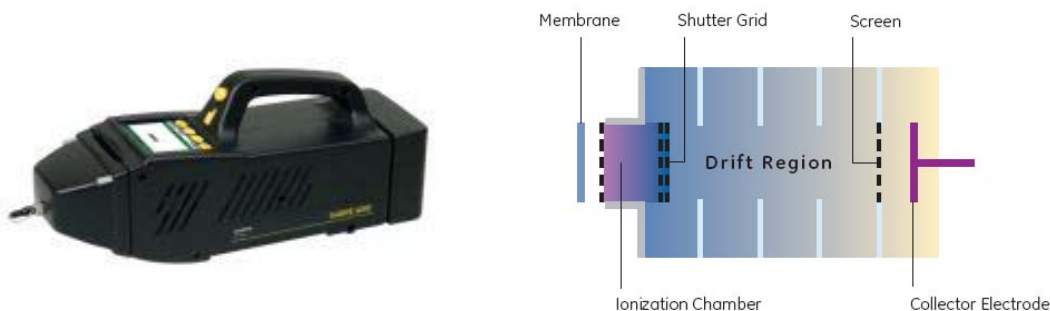


Figure 4: The picture on the left is the Smiths Detection Sabre 4000 handheld IMS-based detection system [8]. The image on the right is an illustration of IMS sensor technology principles. [7]

IMS can be augmented to accept both vapor and particulate matter. In either case, the sample is vaporized and sent into the ionization chamber, illustrated in the right image of Figure 4. While in the ionization chamber, an ionizing source emits low-energy beta particles, resulting in positive and negative ion formation in the gas phase. The shutter grid—a gating mechanism—allows either positive or negative ions to pass through and enter the ion drift region where an applied electric field accelerates them. The latest developed systems can detect both positive and negative ions, called dual-mode. This capability may prove helpful as the number of substances of interest expand. Most IMS systems offer low duty cycles that allow less than 1% of the ions created in the ionization chamber actually reach the drift tube. The remaining 99% of the ions are discharged on the shutter grid. This inefficiency prohibits limit of detection improvements. The rate at which these ions cross the ion drift region is inversely proportional to the mass and collision cross-section of the ion. This correlation allows for the identification of the target substance [7]. Recent advances in IMS technology described by Moore [1] include optimized ionization for explosives and micro-Faraday detector array development. Typically, a radioactive Ni source is used to ionize the vapors although other sources such as corona discharge, laser ionization, and electrospray ionization are being investigated. [3]

6.2.2 Ion Trap Mobility Spectrometry (ITMS). ITMS technology theoretically enhances the performance of traditional IMS. Similar to IMS, ITMS ionizes vapors and then measures the mobility of the ions in an electric field. The vaporized samples enter an ionization chamber where an ionizing source emits low-energy beta particles, resulting in ion formation in the gas phase. [7]



Figure 5: The picture on the left is the GE Security MobileTrace ITMS detection system. The image on the right illustrates the detection concept for ITMS. [7]

ITMS offers an enhancement by eliminating the shutter grid and the associated loss of ions and sensitivity. With ITMS, ionization reaches equilibrium in a field-free region and is then pulsed into the drift tube where an electric field guides the ions to the collector. As illustrated in Figure 5, removal of the shutter grid allows a much greater number of ions into the drift tube. The increased duty cycle and sensitivity over IMS produces less loss of ions to the shutter grid with its non-equilibrium ionization. ITMS detectors increase ionization efficiency, the main factor in determining detection sensitivity [7]. With higher ionization efficiency, ITMS will still need to handle the increased amount of potential interfering compounds. In real world Army applications, both IMS and ITMS sensor systems could suffer from excessively large samples entering the system and contaminating the detector. The embedded sensing element is not simply replaceable although newer versions could be modified to solve this issue.

6.2.3 Amplifying fluorescent polymers (AFPs). AFPs are capable of extremely low limits of detection of equilibrium explosives vapors, although the families of nitroaromatic compounds (TNT, DNT, etc.) are preferential binders. The ability to transport optical excitations over large distances allows these conjugated polymers to produce gain in fluorescence-based sensing. AFP consists of fluorescing chromophores linked together in polymer chains. When stimulated by light of the correct wavelength, AFP will fluoresce. Molecules with high reduction potential will bind to the AFP and quench the brightness of the fluorescence. [6]

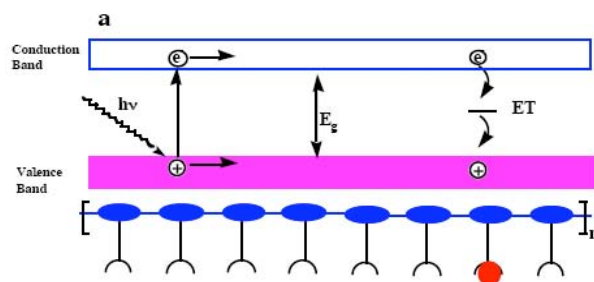


Figure 6: A schematic illustration of the signal amplification. AFPs act as wide bandgap (large E_g) semiconductors, where the molecular orbitals of the repeating units combine to form a continuum, or energy band. Absorption of one or more photons promotes an electron from occupied orbitals in the valence band to the unoccupied orbitals in the conduction band. The now high-energy electron is bound to the empty state in the valence band to produce what is referred to as an exciton. These excitons can radiatively recombine to emit a photon or if they encounter an analyte capable of accepting an electron they are deactivated by an electron transfer process. [6]

The inherent structure of the chromophore chain in AFP dramatically amplifies the quenching effect, resulting in ultra-low detection limits. Conventional fluorescence sensing by quenching involves only the chromophore to which the explosive molecular analyte binds, whereas AFPs involve quenching the fluorescence of many chromophores by a single molecule. The dramatic amplification of response and resultant sensitivity opens potential application for sensor developers. [6] Future efforts to improve sensitivity involve incorporating lasing effects within the polymer material. Very stable polymers

would be needed to promote population inversion and have been discussed by Thomas III and Swager in [12].



Figure 7: From left to right; the first image is an illustration of the sensing element within the Fido technology. The second picture is the handheld Fido XT sensor system that is available as COTS used in many applications. The third image is from the ICx technologies marketing brochure that demonstrates the capability to remotely deploy Fido-based sensor systems. [6]

The ICx Nomadics' Fido sensor, shown in center of Figure 7, is based on an AFP invented by Professor Swager of Massachusetts Institute of Technology (MIT). In the Fido systems, AFP is coated inside the bore of a glass capillary, called a sensing element, which is then inserted into the detector. As shown in the left image of Figure 7, ambient air is pulled through the bore of the sensing element allowing explosive vapors into the air-stream to adsorb on the AFP causing quenching. The response is reversible, so a single sensing element may be used to sample numerous targets throughout its lifespan. There has been extensive testing of the Fido system for DHS and DoD applications. Further advances are widening the range of detectable materials expanding operational uses. [6]

6.2.4 Raman scattering spectroscopy (RS). RS is a method involving probing the molecular structure of unknown materials by analyzing the interactions of light with the sample's chemical bonds. Unlike infrared (IR) spectroscopy (Figure 8), which relies on the direct absorption of low energy, broadband light into vibrational states of the molecule, RS involves the inelastic scattering of high-energy, monochromatic light off the molecules of the sample. As the laser light's electromagnetic field interacts with the molecular bonds, a small fraction of the scattered photons lose some of their energy and are longer in wavelength than the excitation laser. This is referred to as Stokes-shifted light. [7]

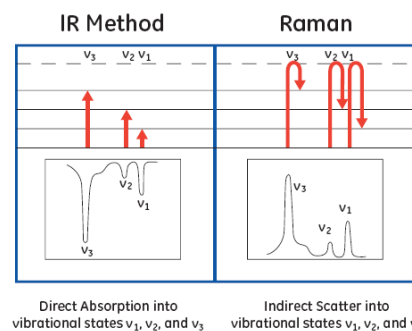


Figure 8: The image on the right distinguishes the differences between IR and Raman mechanisms. [7]

In contrast, if the particular vibrational mode is already in an excited state, typical at higher temperatures, the scattered photon may acquire energy and have a shorter wavelength than the incident laser light. Such scatter is known as Antistokes-shifted light. Each Raman active bond in the molecule causes the emission of a different wavelength of light. Thus, while the light incident on the sample has one wavelength, the light scattered off the sample has many, which carry the information about the identity of the sample. Scattered photons are then collected through a lens and sent to a detector. The collected photons create a pattern of peaks. Each peak is associated with a different bond in the molecule. The spectral pattern, unique to each substance, is compared to a library and best correlated match is the most likely result [7].



Figure 9: The picture on the left is General Electric (GE) Security's StreetLab Mobile Near-Infrared Raman detection system [7]. The picture on the right is the Ahura Scientific FirstDefender Raman Spectroscopy system. [5]

Comparing Raman and IR, the IR spectrum is dominated by vibrations from polar functional groups, while Raman in general is dominated strongly by skeletal vibrations. Skeletal vibrations are very much dependent upon the structure of individual molecules and, as such, Raman spectra tend to be highly individualistic in nature. Therefore Raman tends to be compound dependent, offering highly selective capabilities. Since characteristic functional group vibrations are very dominant in the IR spectrum, families of compounds, which have highly absorbing polar bonds, are recognized readily from repetitive signatures in their IR spectra, such as NO_x. Differences arise in intensity and it is common that a strong vibration in the IR spectrum is weak in Raman and vice versa. Hence, they are considered complimentary sensing techniques. [5]

Standoff capabilities for Raman are currently being investigated although stokes and antistokes mechanisms makeup only a small fraction of the scattered light, which is isotropically emitted. The reality of such low number of available photons hinders sensitivity of RS. One benefit of RS is the ability to create spectra in the presence of water. Water is a weak Raman scatterer and therefore contributes weakly to the spectrum. This is contrary to the limitations imposed on IR absorption spectroscopy, which can be observed by many strong harmonics from the O-H stretching and bending modes.

6.2.5 Gas Chromatography – micro Electron Capture Detector (GC- μ ECD). GC- μ ECD is a well known and widely used laboratory chemical trace analysis technique. GC- μ ECD consists of two major components, the separation process (GC) and the detector (μ ECD). Many other detectors are designed for the GC interface, such as flame

photometric detector (FPD), photo ionization detector (PID), and mass selective detector (MSD). GC- μ ECD works by injecting the dissolved analyte of interest into a vaporization chamber where gas flow forces the sample into a capillary column. The sample enters the column and adsorbs onto the interior wall, or stationary phase, due to drop in temperature. The temperature of the column is then ramped at controlled rates where compounds selectively desorb and flow through the column to the detector. Material identification is only completed when a calibrated response with known sample has been performed prior to an unknown sample. While great selectivity and sensitivity can be achieved, fieldability of this technique has not been easy to realize. Many sensor developers have attempted to integrate a GC-separation stage prior to sensing in order to improve performance and results are still pending. Real world samples that include many different compounds can present resolving problems that require intelligent control.

6.2.6 Mass Spectrometry (MS). MS is a widely used laboratory trace analytical technique that provides high sensitivity and selectivity. The technique separates parent and fragment ions by their respective mass-to-charge ratio and identifies them by manipulating their geometric path to the detector. Many different ionization sources can be applied to MS. Typical laboratory systems operate in a vacuum to reduce mean-free path and collisions although some systems have shown effective atmospheric pressure ionization. Moore [1] describes multiple MS systems that have published results of explosives analysis. There have been recent efforts to make more portable and field-friendly systems, although the required vacuum for ion path and detection may limit fielding systems with unfavorable SWAP attributes.

6.3 Novel Sensor Platforms

As nascent and novel sensing technologies develop, it is clear that new sensor platforms are needed to accommodate new micro- and nano- scale sensors. In addition, as new sensory materials are discovered, creative transduction of sensor response will be needed. The following overview describes recent published articles detailing new sensor platforms. Some industries driving new miniature sensor development are healthcare, automotive, improved safety/EPA standards for hazardous waste handling, consumer electronics, homeland security, etc.

Another very important factor to assess trace sensor technology involves understanding the front-end sampling mechanism. This factor most directly impacts physical sensing techniques that often require a particle sample from the environment be injected into an ionization chamber or active surface for analysis. Senesac and Thundat [18] have identified sample collection as the most challenging task for trace explosive detection. In addition, the ability to preconcentrate the sample has been typically required large amounts of power and long response times. Many chemical analytical methods that perform well in the laboratory, such as nuclear magnetic resonance (NMR), cavity ring-down spectroscopy (CRDS), among others, require meticulous preparation of the sample prior to analysis. In some cases, a vacuum chamber is needed to achieve the required sensitivity and resolving power. These attributes make it difficult for field use of these technologies due to the importance of front-end sample acquisition and processing.

Integration of front-end sampling systems is typically co-designed with the sensing module due to expertise of the sensor developer. Establishing government/industry interface standards in this area may have future payoff.

6.3.1 Microfluidic sampling. Developing lab-on-a-chip devices, front-end sampling is an important step in improving separation of target analyte from background. Zhao et al [62] used electrowetting-on-dielectric (EWOD) actuations to perform droplet manipulation and microparticle sampling on perforated microfilter membranes. In this work airborne microorganisms are identified and quantified, following the two major procedures of sampling and analysis. They split the particle sampling procedure into two sub-processes of particle collection and absorption. First, filter membranes are often used for particle collection, and then the collected airborne particles are absorbed into a liquid solution prior to the analysis procedure since most bioanalytical methods are performed in a liquid phase. Bubbler or impingers can be utilized if the simultaneously execution of collection and absorption are desired.

The process described by Zhao begins with applying air suction through a microfilter membrane to collect airborne particles. These airborne particles of interest, larger than the filter hole size, are stopped and collected on the microfilter membrane. Then a liquid droplet is moved around on the microfilter membrane by sequentially activating an array of embedded electrodes (by EWOD principle), picking up the particles on the microfilter surface and absorbing them into the droplet itself. In this process, the surface tension in the moving droplet is responsible for detaching the particles from the surface. Finally, the droplet containing the absorbed particles can be transported automatically to the adjacent lab-on-a-chip analysis system, also by EWOD actuation. Figure 10 below illustrates the generic process including particle sampling, absorption, EWOD activation to ‘push’ the droplet, and analysis of target analyte in the droplet. [62]

This process allows for an integrated system to provide advantages over current sensing systems. First consumables are minimized due to small droplet volume size. Second, the EWOD operation requires fewer handling steps during particle collection and minimizes sample loss, which is a key factor for analysis of explosive airborne particles due to their low vapor pressure as well as small amount of solid sample available on surfaces. Lastly, this process is able to run continuously allowing for more reliable performance given Army applications. [62]

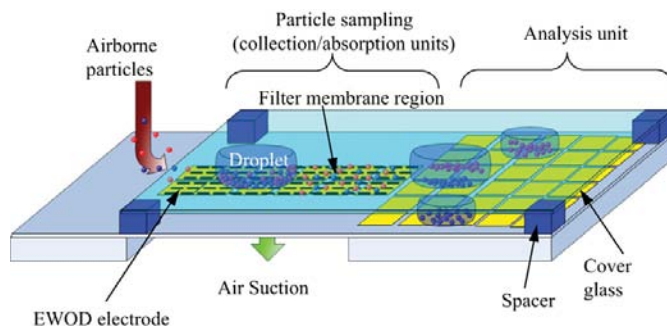


Figure 10: Microfluidic sampling and analysis process incorporating the electrowetting-on-dielectric (EWOD) principle. [62]

Conclusion: Conventional systems designed for collection and absorption of airborne particles are generally bulky, requiring not only a large volume of liquid in impinging particles into liquid or extracting collected particles from filter surfaces but also numerous manual handling steps. Thus, they are not typically compatible with the miniaturized lab-on-a-chip system. In the meantime, the lab-on-a-chip system may bring many advantages over conventional analytical technologies: short processing time, drastic reduction in reagent and sample consumption, small mass of equipment, full automation, high throughput, highly sensitive and specific output signals. However, seamless integration of lab-on-a-chip devices with the existing particle collection/absorption systems remains a challenging issue due to the immense amount of background or interfering chemicals that are inherently consumed and processed by high duty cycle sampling systems. Continuous sampling and analysis would be well-desired technological advance for microfluidic systems to improve field readiness and user confidence.

6.3.2 Micro-preconcentrator. Researchers [76] at the Naval Research Laboratory (NRL) have designed and fabricated a micro-preconcentrator device using complementary metal-oxide semiconductor (CMOS) technology. The fabricated device is essentially a suspended microhotplate design that is configured to allow airflow through the device in a direction perpendicular to the plane of the device. This preconcentrator device is designed to integrate in front of current COTS vapor detection systems. The complete preconcentrator was configured as an array of 225 angled bridges. A set of five angled bridges are released via backside etch and the heaters are electrically connected in parallel, as shown in the first image of Figure 11. The complete device has 45 pits to allow airflow through the device (middle image in Figure 11). A sorbent polymer (known as HCAS2) was coated on the microhotplate surface in order to trap and collect the vapor or gas of interest, which is capable of withstanding operating temperatures of approximately 180 °C. The sorbent polymer is used to collect and concentrate analyte at ambient temperatures by maximizing vapor-trapping efficiency. Then, rapid heating of the microhotplate delivers analyte to the intake of the integrated COTS sensor. They were able to determine thermal rise time of the microhotplate to be 40 milliseconds (ms) showing agreement between experimental and theoretical. After a given sampling time, a thermal desorption cycle is then used to rapidly heat the preconcentrator to 180 °C to release a concentrated wave of analyte. [76]

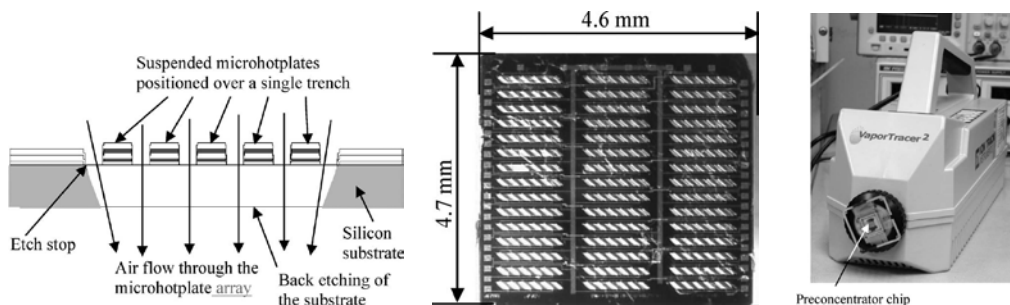


Figure 11: Sorbent polymer coated microhotplate preconcentrator. Hotplate fabrication design on left, actual size preconcentrator chip in middle, and interfaced chip with COTS sensor. [76]

The device was evaluated by testing with nerve agent stimulant dimethylmethylphosphonate (DMMP) and explosive 2,4,6-trinitrotoluene (TNT) vapors. The preconcentrator device was demonstrated by interfacing to the front end of a handheld chemical agent detector and a handheld trace explosives detector, the GE Vapor Tracer 2, as shown in right hand image in Figure 11. These preliminary experiments demonstrated a six-fold sensitivity enhancement after thermal desorption of collected DMMP vapor and a threefold sensitivity enhancement after thermal desorption of collected TNT vapor. [76]

Conclusion: The microhotplate designed preconcentrator offers a means to improve capabilities of current COTS and novel vapor sensors. The rapid temperature increase allows fast cycle times helping users. The paper mentioned enhanced sensitivity with DMMP and TNT with the stated sorbent polymer. It is unclear how effective this polymer would be against other families of explosive compounds. Perhaps an array of microhotplates with various sorbent polymers specific to many explosives would enhance sensor response. With regard to Army applications, testing would need to be performed involving airborne particulates and potential interfering compounds.

6.3.3 Ion mobility – mass spectrometers (IM-MS). As mentioned earlier, IMS has been widely deployed by DHS and TSA. In addition, MS has been the gold standard for many years in laboratory chemical analysis. As researcher develop more field usable detection systems with the combination of these two technologies, IM-MS may likely be capable to provide Army solutions. Kanu et al [48] compares and contrasts various types of IM-MS available today and describes their advantages for application to a wide range of analytes. IMS, when coupled with MS, offers value-added data not possible from mass spectra alone. Given an improved particle and vapor collection mechanism, ion mobility cells coupled to mass spectrometers offers improved separation, reduction of chemical noise, and measurement of ion size are possible. Difficulty occurs in traditional mass spectrometers when structurally similar ions and ions of the same charge state land on the detector. By including the ion mobility stage prior to the mass spectrometer, the sample can be separated into families of ions which appear along a unique mass-mobility correlation line. Kanu's review describes the four methods of ion mobility separation currently used with mass spectrometry in the laboratory environment. They are (1) drift-time ion mobility spectrometry (DTIMS), (2) aspiration ion mobility spectrometry (AIMS), (3) differential-mobility spectrometry (DMS) which is also called field-asymmetric waveform ionmobility spectrometry (FAIMS) and (4) traveling-wave ion mobility spectrometry (TWIMS). DTIMS provides the highest IMS resolving power and is the only IMS method which can directly measure collision cross-sections. AIMS is a low resolution mobility separation method but can monitor ions in a continuous manner. DMS and FAIMS offer continuous-ion monitoring capability as well as orthogonal ion mobility separation in which high-separation selectivity can be achieved. TWIMS is a novel method of IMS with a low resolving power but has good sensitivity and is well integrated into a commercial mass spectrometer. [48]

Conclusion: As IMMS instruments become more commercially available and move from the research and development laboratory to the applications laboratory, the mobility

advantage in mass analyses will continue to grow in importance. The benefits include improved sensitivity, quantification, resolving power and separation selectivity by the addition of mobility to mass measurements and create a powerful analytical tool for the analysis of complex mixtures. In order to realize these benefits, developments in higher-order differential ion mobility separations, multidimensional IMS, dense-phase IMS, novel interface technologies, and ionization sources will be needed. With regard to Army applications, it may be more difficult to realize these type systems in a field environment. Most ion mobility cells would need to operate at atmospheric pressure causing increased difficulty when interfacing to mass spectrometers that need to be under vacuum to realize the benefits mentioned above. In addition, there are many components and complex systems that elevate size, weight, and power requirements. [48]

6.3.4 Sub-surface ion mobility spectrometer. In order to find potential solutions to chemically sense explosives in a field environment, one may look to successful systems designed for monitoring environments for volatile organic compounds (VOCs). Sevier et al [49] reports on a new sub surface IMS to provide cost effective real time monitoring of VOC contaminated sites, which has been developed by an interdisciplinary team from Boise State University and Washington State University. The sensor system, which completely fits with a 2 inch diameter, ~2 foot long housing, consists of a sampling tip, sampling module, IMS sensor, trans-impedance amplifier, and high voltage electronics. The system is designed to be deployed below ground although it must be interfaced to an above ground field box consisting of flow control system and data acquisition. These sub-systems combine to provide the first IMS sensor that can be deployed in the subsurface to sample and analyze soil gas VOCs. [49]

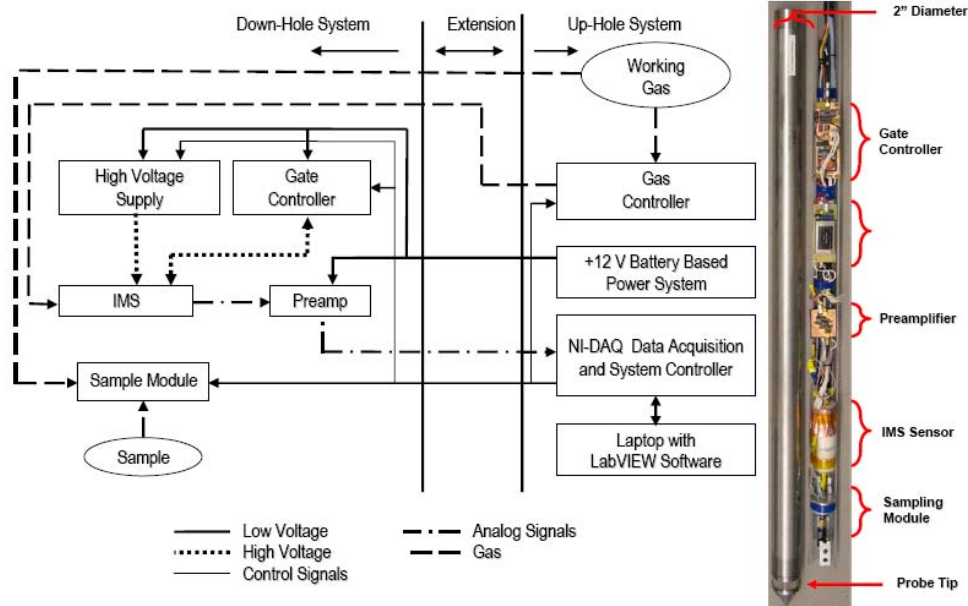


Figure 12: Configuration (left) and actual sensor (right) of the IMS probe system. [49]

Figure 12 above illustrates the specific components as well as the shape of the IMS probe. The IMS probe system consists of three major subsystems: the down-hole probe

system that includes the IMS sensor and associated electrical and gas flow systems, the up-hole system consisting of a power data acquisition and control, stand alone power supply and gas control system and the extension system which is used to interconnect the down-hole to the up-hole systems. [49] The probe has been tested in the field at multiple locations and depths ranging from 5 - 20 ft below the ground although the sensitivity was not clearly demonstrated. The main focus of the research was to demonstrate that the system can function in the subsurface.

Conclusion: The researchers [49] have developed and tested a sub-surface IMS probe for analysis of VOCs. They have identified future work that will focus on incorporation of a multicapillary column to enhance analyte identification through chemical separation. Army applications could benefit from the lessons learned in miniaturization and stream lining the components. Confirmation of partially buried or concealed explosive targets may be a suitable application for this type of sensor design. Additional applications include hard-to-reach headspace volumes for robotic platforms. The flow control and data acquisition box interface would need to be enhanced, although this design seems well suited for real world field applications.

6.3.5 Hadamard Transform Ion Mobility Spectrometry (HT-IMS). Yet another enhancement to IMS that may provide capability to resolve low vapor pressure explosives is based on Hadamard Transform (HT). The spectrum acquired using traditional ion mobility spectrometry (IMS) is an average of multiple experimental cycles. Ions are created and remain in a chamber until initiated by passing a short burst of ions through a gate into a drift tube containing a homogeneous electric field. As the gate opens and closes, multiple cycles allow ions in the system to be subjected to the electric field and separate based on ion size. To reduce spectral overlap, each separated ion group drift time measurement must be completed prior to initiation of the next sequence. To maximize resolution, the ion pulse admitted to the drift tube is small in relation to the total scan time with the unfortunate consequence of an inherently low duty cycle (<1%). Unfortunately, simply increasing the duty cycle by lengthening the gate pulse degrades the resolution, which results in sacrificing throughput and sensitivity in order to meet resolution requirements. [47]

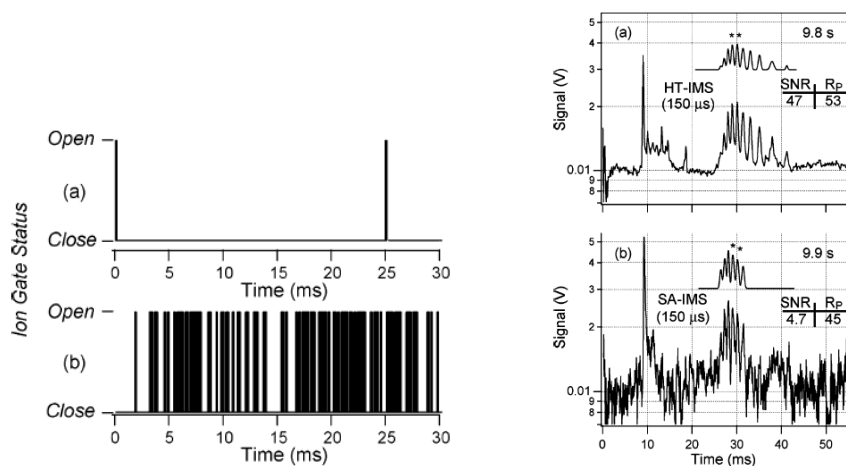


Figure 13: Illustration of the improved duty cycle (left) and signal-to-noise ratio (SNR) (right) for HT-IMS. The left image compares the duration of gate opening for typical systems (above) to the HT systems (below). The right image compares (SNR) of the same sample using HT-IMS (above) and typical signal averaged (SA-IMS) (below). [47]

Clowers et al [47] implemented HT to provide the benefits of an increased duty cycle and improved SNR when compared to signal averaging techniques. The Hadamard transform utilizes a binary series, in this case, a series of open and close pulses applied to the Bradbury-Nielson (B-N) gate, followed by deconvolution to realize the multiplexing advantage. Specifically, Clowers group implemented Hadamard transform IMS (HT-IMS) in which the B-N gate is modulated in accordance with a known series of pulses, effectively producing many ion packets that intermingle in the separation region. The signal acquired during an HT-IMS experiment is thus a superposition of drift spectra, and according to the properties of Hadamard transforms, the duty cycle of IMS is increased to 50%. To retrieve ion mobility drift spectra, the superimposed signal is deconvoluted with the inverse of the applied transform. [47]

Conclusion: According to the initial results of Clowers paper [47], measurements of amphetamine and cytochrome samples indicate a 2-10-fold increase in SNR for the HT-IMS technique with no reduction in resolution. From the limited studies using HT, it is not clear how explosives analysis may be improved, although offering an improved SNR through a 50% duty cycle represents a fresh alternative to typical signal-averaged data acquisition. Due to complex mixtures that are present in field environments, it is possible for this technique to improve sensitivity and selectivity, although HT-IMS has yet to show any results from field implementation in the literature.

6.3.6 Microcantilevers. Recent advances in the fabrication of silicon-based microcantilever beams allow for detection of extremely small stress and absorbed mass leading to development of miniature explosive vapor sensors. Microcantilevers offer three different sensing mechanisms to detect vapors. The first approach involves coating the cantilever beam with a selective layer that causes a bending of the cantilever upon adsorption of explosive molecules. The key aspect to this sensing mechanism is the adsorption of analyte to a single side of the beam, or if there is a differential adsorption on opposite sides. Adsorption-induced forces, caused by a reduction in free energy at the surface, should not be confused with bending due to dimensional changes, such as swelling of the polymer films on the beams. [77] The beam deflection changes as a function of absorbate coverage. The relation between beam bending and changes in surface stress are described in Stoney's formula and the Shuttleworth equation,

$$\frac{1}{R} = \frac{6(1 - \nu)}{Et^2} \delta s \quad \sigma = \gamma + \left(\frac{\delta \gamma}{\delta \varepsilon} \right) \quad [77]$$

where R is the radius of curvature, t is the thickness of cantilever, ν and E are Poisson's ratio and Young's modulus. δs is the differential surface stress, which is related to the surface stress, σ , surface free energy, γ , and surface strain, $\delta \varepsilon$. These relations show the deflection of the cantilever is directly proportional to the adsorption-induced differential

surface stress. The sensitivity of adsorption-induced surface stress can be orders of magnitude higher than frequency-variation mass sensors. [77]

Various receptor coatings have been widely studied to enhance the selectivity by preferentially binding explosive molecules. The key factors leading to enhanced selectivity are molecular affinity and fast regeneration, or reversibility. Weak chemical bonds can be unselective by nature, such as van der Waals and hydrogen bonding. However, when manipulating these interactions in an array format a more effective sensor can emerge. Moore [31] and Senesac [18] identify functionalized self assembled monolayers (SAMs), metalloporphyrins, molecular imprinted polymers (MIPs), metal oxides, among others as candidates for selective coatings for micro- and nanocantilevers. These partially selective coatings have lead to detection limits of 20 parts-per-trillion (ppt) of TNT by volume and 10-30 ppt of RDX and PETN. [17, 31]

The second sensing mechanism is strictly based on frequency variation due to change in mass of the cantilever beam. Assuming the adsorbed vapor molecules have no impact on the spring constant, the adsorbed mass can be determined from the change in resonance frequency and the initial cantilever mass from

$$\frac{f_1^2 - f_2^2}{f_1^2} = \frac{\Delta m}{m} \quad [77]$$

where f_1 is the initial and f_2 is the final frequency, respectively. m is the initial cantilever mass and Δm is the adsorbed mass. As the relation demonstrates, sensitivity of mass sensing microcantilevers can be improved by increasing the resonance frequency and decreasing the initial mass (nanocantilevers). Therefore, this detection mechanism alone is not currently suitable for sensing explosive vapors. [77]

The third sensing mechanism involves thermal effects. Due to low thermal mass of the microcantilever beams, rapid heating can cause deflagration of any adsorbed energetic material resulting in additional heat-induced bending of the beam. [77] Deflagration is an exothermic process causing differential bending that is clearly distinct from endothermic processes such as melting, vaporization, and decomposition. The sticking coefficient of explosive molecules plays a role in allowing deflagration to proceed, which can reduce effects from interferents. Senesac [18] and Datskos [77] have quoted detection limits at approximately 50 picograms for TNT using the deflagration method. This mechanism is highly transient and relies heavily on uniform distribution of adsorbants. Deflagration also provides a means to ‘clean’ the cantilever beams after each cycle.

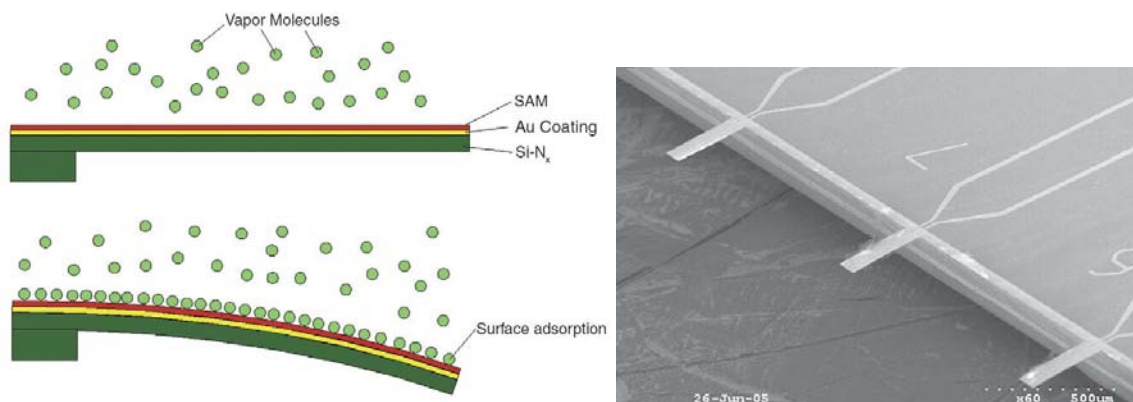


Figure 14: Depiction of microcantilever (left) before and after vapor adsorption on the coated surface. Microcantilever sensor array (right) allowing for multiple coated and uncoated beams to allow for background subtraction. [18]

The use of current receptive coatings (SAMs) on a single cantilever beam will not create the needed selectivity because the fundamental mechanism is an acid-base reaction, causing many false alarms. Creating an array of beams with varying receptors may provide orthogonal signals although costs will inherently increase. Unique responses could be obtained for explosive molecule interactions using pattern recognition techniques. [77] This electronic nose concept has been studied for many years and has had success when identifying the presence of one chemical. Difficulties arise when multiple components are desired to be detected resulting in decreased sensing confidence levels. This decrease is most likely due to the limited number of interactions available as more cantilever beams are added to an array. [18] Improved detection limits could be achieved with smaller spring constants and lower thermal mass. [77]

Singh [17] and others have stated microcantilever sensor platforms are amenable for remote monitoring and do not require sample preparation. In order to increase the number of interactions it may be beneficial to improve sample collection (vapor and particles), preconcentration, and presentation to cantilever arrays. Perhaps a batch cycle mechanism instead of continuous vapor stream may enhance interactions and pattern recognition capabilities. Regardless of front end sampling improvements, it is clear more work is needed to make microcantilevers more discriminating of explosives from chemicals typically found in Army sensor applications while ensuring receptor coatings do not require extended time to regenerate.

Conclusion: Microcantilver sensing platforms satisfy many requirements for Army applications. They offer extremely high sensitivity, low power consumption, real-time operation and miniature size. They are also compatible with array arrangement for simultaneous detection. As more receptive coatings are discovered, selectivity should improve and more harsh condition applications can be tested. One disadvantage is the possibility that added noise from field use may cause higher background signal.

6.3.7 Surface Acoustic Wave (SAW) sensors. Surface acoustic wave (SAW) signal-processing devices such as delay lines and resonators impart chemical sensitivity by a thin adsorbent coating on the surface of the SAW device. Proper adsorbent films allow

for high sensitivity and selectivity to detect gases or vapors of interest. These sensors can be used for detecting hazardous gases, chemical warfare agents, explosive vapors, environmental pollutants as reported in multiple publications [81-84]. Detection limits in the range of ppm and ppb are reported for gas and vapor sensors. Reversibility and reproducibility is achieved since the vapor interaction is through surface adsorption and desorption. Upon adsorption, the mass loading by vapor molecules causes change in the SAW characteristics such as attenuation and velocity, which in turn affects the amplitude, delay and phase of the SAW device. With real world conditions, other physical and environmental variables such as temperature, sample gas flow and strain/stress also cause change in SAW characteristics. In order to ensure extraction of the chemical signal from these interferences, a dual device mode sensing is employed. [81] In this case, a reference uncoated identical SAW device is placed next to the coated sensor device and exposed to identical conditions. Taking the difference in the frequency shifts of these two oscillators minimizes the effects of spurious factors. Maximizing this frequency shift is the driving force behind sorbent film choice.

McGill et al [82] reported on a series of hexafluoroisopropanol (HFIP) functionalized aromatic siloxane polymers have been synthesized, characterized, and evaluated as vapor sorptive coatings for use with chemical sensors. These strong hydrogen bond acidic (hba) polymers readily and reversibly sorb hydrogen bond basic (hbb) vapors such as nitroaromatics. Based on a SNR of 3, they determined the detection limit for 2,4 DNT vapor with a 250-MHz SAW device coated with the siloxane polymer (SXPHFA) to be approximately 235 ppt. The SAW devices were utilized as a tool to evaluate the sorption properties of new and old polymers synthesized at NRL. [82]

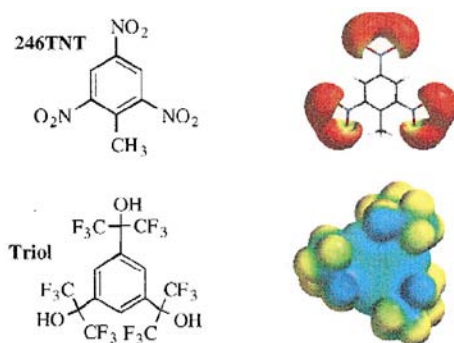


Figure 15: Chemical structure (left) of TNT and Triol; and electron rich sites (right) with complementary hba and hbb sites.

McGill et al [82] described the important parameter that quantifies the sorption of a vapor in a polymer coating, called the gas–polymer partition coefficient, K_p . This parameter is defined as the ratio between the concentration of the vapor in the gas phase, C_v , and the concentration of the sorbed vapor in the polymer phase, C_p , at equilibrium. For vapor–polymer partition coefficient, the salvation equation is given by the linear solvation energy relationship (LSER), [82]

$$\log K_p = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l\log L^{16} \quad [82]$$

where $\log K_p$ is the log of the gas–polymer partition coefficient, and relates to a series of vapors for a polymer. It measures the strength of the interaction between vapor molecules and polymer molecules. Larger K_p values indicate that the vapor molecules are more soluble in the polymer solvent phase. The variables are solute vapor parameters: R_2 , an excess molar refraction that models polarizability contributions from “n” and “p” electrons; π_2^H , the dipolarity/polarizability; α_2^H , the hydrogen-bond acidity; β_2^H , the hydrogen-bond basicity; and $\log L^{16}$, where L^{16} is the gas–liquid partition coefficient. The coefficients resulting from a regression of $\log K_p$ values characterize the solubility properties of the polymer. The most important of these are: s , the dipolarity; a , the hydrogen-bond basicity; b , the hydrogen-bond acidity; and l , which reflects a combination of solvation cavity effects and dispersion interactions. The magnitude of “ l ” reflects the ability of the polymer to discriminate between a compounds of similar structure. The coefficient “ r ” reflects the polarizability of the polymer, and “ c ” is a constant resulting from the regression. The size and relative magnitude of all the coefficients are used to identify polymers with high selectivity and sorption characteristics for vapors or gases of interest. McGill et al considered a wide range of chemoselective polymers and characterized them with the LSER equation. [82]

Kannan et al [84] experimented with a strongly hydrogen-bond acidic that readily and reversibly sorbs nitroaromatics called carbowax. They dissolved carbowax in methanol and coated it on 150 MHz devices with the density of 0.33 g/cm². The adsorption in the lower concentrations was slightly lower and some vapor remained in the gas stream as unabsorbed, while as the concentration increased the adsorption efficiency also rose to around 83%. The sensor was found to be sensitive and gives linear response in the ppb range.

Kapoor et al [83] reported on a number of polymers for their use as sensing polymers for nitroaromatics for the detection of explosive vapor-sensing SAW, use of various adsorbent materials such as carbowax, quadrol, fluoropolyol, and its modified compound, SXPHFA and SXFA. The most sensitive of the new polymers that Kapoor reported exhibit SAW sensor detection limits for nitrobenzene and 2,4- dinitrolune at 3 ppb and 235 ppt, respectively. Coating different polymers on the same device was also studied. Poly- dimethylsiloxane was used as a sensing material for TNT using 37 MHz SAW devices and the frequency shift observed was 10 Hz/ppb. In another study [83], the same 37 MHz device was used with carbowax for the detection of TNT vapors, which resulted in a response of 8Hz/ppb at room temperature. Thin-film bulk acoustic wave resonators have been used and demonstrated detection limits of approximately 5 ppb for TNT vapors.

Nimal et al [81] compared in-house made and commercially available SAW devices for use in sensor systems. Various types of SAW devices (delay line, dispersive delay line, filter and resonator) were compared with operating frequencies between 36 and 434 MHz. Polymer coatings were chosen based on their selectivity toward explosives and chemical warfare agents (CWA). The dispersive delay line sensor offered lowest sensitivity and higher stability. SAW devices on Quartz, LiNbO₃ and ZnO/glass substrates are used. Quartz-based SAW devices are preferred for their low temperature

sensitivity. Determining LOD for each sensor was not one of their goals, they were able to achieve 3 ppb of sarin (CWA) in nitrogen gas which corresponded to other literature. For common explosive ERC, 2,4 DNT, they only tested down to hundreds of ppb.

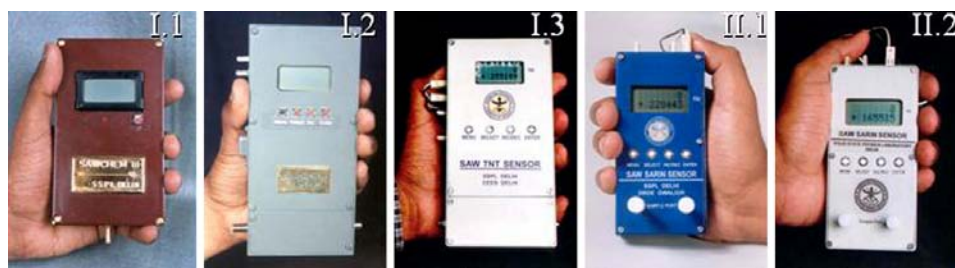


Figure 16: Various laboratory fabricated and commercially available SAW sensors tested by Nimal et al [81].

One key observation, the placement and packaging of the SAW devices in the sensor cell is found to be the key parameter in determining the baseline stability apart from the individual oscillator stability. It was found that the two SAW devices on the same chip is the optimum arrangement for maximum baseline stability. The sensitivity is found to be more for sensor systems with higher oscillator frequency. However, it is also suspected that higher the phase slope or group delay lower is the sensitivity. Although all performed well, they concluded advantages and disadvantages should be considered beforehand for the targeted application. [81]

Chuanzhi et al [37] reported on a novel analytical system based on high Q-value ($Q = f_0/\Delta f$) SAW resonator array and probabilistic neural network (PNN) was developed to detect chemical warfare agents or simulant. The fabricated array consisted of four two-port SAW resonator sensors with a fundamental frequency (f_0) at 200 MHz. To improve the selectivity and sensitivity, four polymers such as polyepichlorohydrin (PECH), Silicone (SE-30), Hexafluoro-2- propanol bisphenol-substituted siloxane polymer (BSP3), fluorinated polymethyldrosiloxane (PTFP), were selected as the sensitive film materials and were coated on the surface of different resonators of the array by spin-coating method. Then, the array was used to detect mustard gas (HD), dimethyl methylphosphonate (DMMP), sarin (GB) and sarin acid. The frequency output of each sensor was mixed with a bare reference device. The signals obtained from the array were analyzed with PNN to identify the target analyte. They identified the correct gas with 90.87% accuracy. [37] They concluded combining SAW resonator array with PNN could detect and identify these gases quite well. Further testing with selective sorbent coatings for explosives could result in improved sensor confidence and most importantly correct identification with gas mixtures.

Conclusion: SAW devices used as chemical vapor sensors are very sensitive, have low detection limits in the ppt and ppb range for some explosives, high dynamic range, fast response times, and can be easily adapted into sensor arrays for improved selectivity. Further work is needed to identify sorbent coatings selective to explosives combined with signal processing techniques as reported by Chuanzhi [37]. Reversibility of the SAW devices would need to be validated as new sorbent coatings are developed, which could affect sample throughput. Size, weight, and power consumption are also advantageous

with SAW sensors although, as with most trace sensors, interfacing particle and vapor sampling would need to be developed and tested.

6.3.8 Carbon nanotubes (CNTs). CNTs have been investigated for many applications since their discovery in the early 90s. The discovery of carbon nanotubes (CNTs) has generated keen interest among researchers to develop CNT-based sensors for many applications. Utilizing CNTs in next-generation of sensors has the potential of revolutionizing the sensor industry due to their inherent properties such as small size, high strength, high electrical and thermal conductivity, and high specific surface area. Recent advances may allow CNTs to act as charge carriers for explosive specific vapor sensing. Their electromechanical properties are very unique and advantageous for microsensor systems. Long-term development plans for small, low cost, low power sensor systems would seem to be a smart application for CNTs.

Sinha et al [85] reviewed CNT based sensors and their applications. Included in their discussion were some basics about CNTs that are essential when understanding their potential benefit. CNTs are hexagonal networks of carbon atoms of approximately 1 nm diameter and 1 to 100 microns of length. They can essentially be thought of as a layer of graphite rolled-up into a cylinder. Depending on the arrangement of their graphene cylinders, there are two broad classifications of nanotubes: single-walled nanotubes (SWNTs or SWCNTs) and multi-walled nanotubes (MWNTs or MWCNTs). SWNTs have only one single layer of graphene cylinders; while MWNTs have many layers (~ 50), as shown in Figure 16 below. [85]

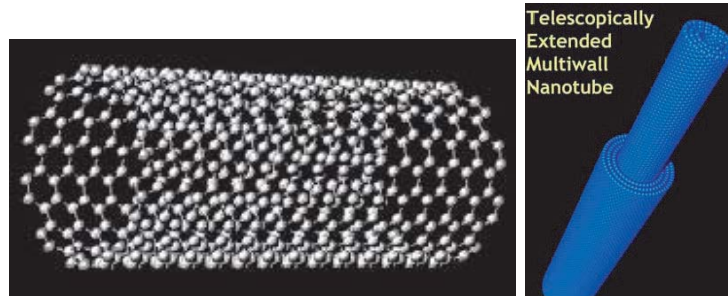


Figure 16: Sheet of grapheme (left) rolled into a single wall nanotube (SWNT). Multiwall nanotube (MWNT) telescopically extended (right). [85]

Furthermore, the films of synthesized CNTs can be aligned or random in nature, directly affecting their sensing mechanism. Although SWNTs are structurally similar to a single layer of graphite (that is a semiconductor with zero band gap), they can be either metallic or semiconducting depending upon the tube diameter and the chirality. The chirality is defined by the sheet direction in which the graphite sheet is rolled to form a nanotube cylinder. The diameter (d) and the chiral angle (θ) can be obtained by an integer pair (n , m) using the following equations

$$d = \frac{a\sqrt{m^2 + mn + n^2}}{\pi} \quad \theta = \arctan \left[-\frac{\sqrt{3}n}{2m + n} \right] \quad [85]$$

where a is the lattice constant (distance between atoms) in the graphite sheet. The relation between n and m defines three categories of CNTs: (i) armchair ($n = m$ and chiral angle equal to 30°); (ii) zigzag ($n = 0$ or $m = 0$ and chiral angle = 0°); and (iii) chiral (other values of n and m and chiral angles between 0° and 30°). [85]

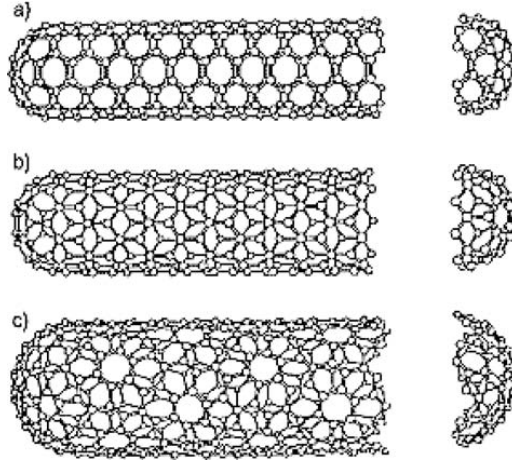


Figure 17: Armchair (a), zigzag (b), and chiral (c) configurations of nanotubes. Specific configurations offer different properties for microsensing. [85]

The above Figure 17 shows all the three categories of CNTs. All armchair nanotubes are metallic, as well as those with $n-m = 3j$ (j being a nonzero integer). All others are semiconductors, which have the band gap that is inversely related to the diameters of the nanotubes. For field effect transistor sensing devices, only semiconducting CNTs are utilized. MWNTs are either nested CNT shells or have cinnamon roll like structure. For the development of molecular electronics, methods have been proposed to separate metallic and semiconducting SWNTs. Difficulties arise during fabrication when separation of chirality is desired. The dielectric responses of the carbon nanotubes are found to be highly anisotropic. The electronic transport in metallic SWNTs and MWNTs occurs with minimal scattering over long lengths due to their nearly one dimensional electronic structure. This enables nanotubes to carry high currents with negligible heating. This points to the potential of CNTs as interconnects in large-scale integrated micro- and nanoelectronic devices. [85]

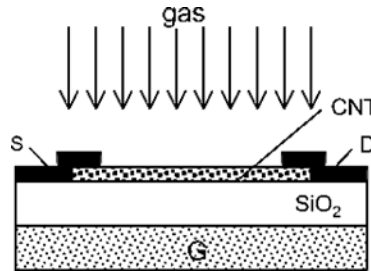


Figure 18: Concept depiction of CNT-based gas sensor including the gate, dielectric, source, drain, CNT matrix and entering gas. [85]

Zhang et al [86] reported on the intriguing gas sensing capabilities of CNTs due to their advantages of high surface area, good environmental stability, and excellent mechanical and electronic properties. The most common route to effectively enhance the sensitivity

and to broaden the scope of analytes to be detected is to functionalize the surface of CNT with specific bio/chemical molecules. Surface functionalization of CNTs with sorbent selective materials is especially attractive for developing explosive sensors for real world field deployment.

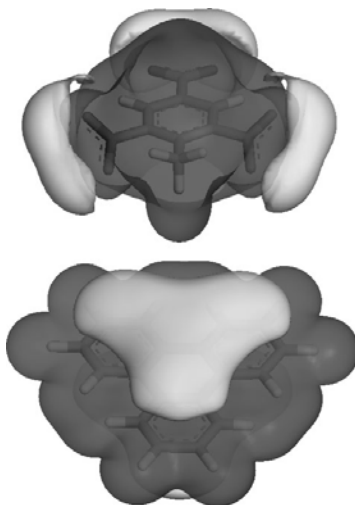


Figure 19: Electrostatic potential animation of TNT (above) and TP (below). [86]

Zhang's group specifically studied this concept using triphenylene -functionalized MWCNTs (TP-MWCNTs) as the sensing unit of TNT. They discovered that TP-MWCNTs demonstrated higher sensitivity and faster response toward electrochemical detection of TNT than that of pristine MWCNTs, which are highly desirable sensing characteristics. The improvement for the sensitivity of TP-MWCNTs to TNT, about 50 times that of MWCNTs, is most likely attributed to the cooperative recognition of TP and MWCNTs to TNT. The attachment of TP on MWCNTs leads to better sensing unit with a more receptive site to TNT, and this may be partly attributed to both significant π - π intermolecular charge transfer and hydrogen bond interaction between TP and TNT molecule, which results from the shape and electrostatic complement between them, as shown above in Figure 19. As in the TP polymer, the ability to transport optical excitations over the backbone of large distances bearing many receptors is the origin of the amplification in fluorescence-based sensors. Zhang et al concluded the attachment of TP on MWCNTs surface brings more receptors on the sensing unit, which is the origin of the improvement in electrochemistry-based sensors. [86]

Hrapovic et al [87] studied metal nanoparticles (Pt-platinum, Au-gold, or Cu-copper) together with MWCNT and SWCNT solubilized in Nafion and used to form nanocomposites for electrochemical detection of TNT and several other nitroaromatics. Among various combinations tested, the most synergistic signal effect was observed for the nanocomposite modified glassy carbon electrode containing Cu nanoparticles and SWCNT in Nafion. This combination provided the best sensitivity for detecting TNT and other nitroaromatic compounds. They concluded the two major contributing factors were the combination of excellent adsorptive properties of SWCNT with an enhanced electrochemical-active surface area and electrical conductivity of Cu. Such nanocomposite-modified glassy carbon electrodes exhibited very good reproducibility

and stability. Hrapovic reported results with a detection limit of 1 ppb for TNT in solution phase, with linearity up to 3 orders of magnitude. Selectivity toward the number and position of the nitro groups in different nitroaromatics was very reproducible and distinct. [87]

Senesac et al [18] discussed electric field effects induced by molecular adsorption and how it can drastically change conduction in nanowires (SWNT, Si, ZnO, etc.). When large potential is applied, the electric field radiating from the SWNTs changes the polarization of the adsorbed molecules directly affecting the measure of capacitance. The capacitance change along with the coating the SWNTs with more chemically selective layer can enhance selectivity of CNTs.

Conclusion: As mentioned above, CNTs offer sensing advantages due to their inherent properties such as small size, high strength, high electrical and thermal conductivity, and high specific surface area. Studies have demonstrated CNTs to act as charge carriers for explosive specific vapor sensing proving their electromechanical properties are very unique for microsensor systems. In addition, fabricating sensor arrays using CNTs should be plausible as more selective materials are developed and tested. With regard to Army applications, CNTs offer potential solutions as their attributes allow them to be flexibly deployed. Interfacing with enhanced sampling may be an engineering challenge but no unlike other vapor/particle sensing platforms.

6.3.9 Lab-on-a-chip. Single microchip platforms able to perform all processes needed in a sensor system have recently been the focus of research [77]. These processes performed by microfabricated microfluidic analytical devices involve sample extraction and preconcentration, separation, and detection within short response times. The miniaturization allows for reliance on electrokinetic pumping eliminating the need for microvalves and micropumps. Networks of microchannels made with various methods and materials are predominantly fabricated on glass or quartz substrates.

There are multiple ways to measure the signal from analytes interacting with the sensing electrode in solution based lab-on-a-chip devices. One way is to control the working electrode at a fixed value and monitor the current over time, or amperometric detection. The applied potential acts as a driving force for either reduction or oxidation reactions to proceed faster. The resulting current reflects the rate at which electrons move across the electrode-solution interface. Observing current as a function of time, peaks represent maximums in concentration of target analyte as the pass through the detector. Easily reducible nitro groups found on nitroaromatic compounds make good candidates for amperometric detection. Collins et al [77] reported detection limits for 1,3-dinitrobenzene (DNB) and 2,4-dinitrotoluene (DNT) at 70 and 110 parts per billion, respectively.

Another means to measure lab-on-a-chip devices, called contactless conductivity detection, has been used for detecting mobile ionic explosives under the influence of an electric field. This method relies on placement of two external metallic electrodes on the thin cover of a plastic microchip to act as a planar capacitor. While operating the

detector with sine wave excitation voltages conductivity changes in the microchannel area below the two electrodes can be monitored. Advantages of this technique, versus contact electrodes, include absence of bubble formation and surface passivation, effective isolation from high separation voltages, simplified construction and alignment of detector, and the use of narrow microchannels. Detection limits have been reported [77] at 100 nanomolar solutions at excitation voltages up to 250 V. Combining both amperometric and conductivity detection has lead to distinct separation and analysis of a seven component explosives related compound mixture in under two minutes. [77]

With regards to optical detection, the most widely used means to measure analyte concentration via lab-on-a-chip is through laser-induced fluorescence (LIF). Its great sensitivity is derived by low background noise and available fluorescent dye tags. Research reported by Collins et al [77] used assays of antigen-labeled antigen-antibody complexes to determine the sensitivity and linear dynamic range of TNT. They established detection limits of ~1 nanogram/milliliter (ng/mL) and a dynamic range of 1-300 ng/mL. In addition, indirect fluorescence has quantitatively measured mixtures of nitroaromatics explosives. Indirect fluorescence relies on quenching and background fluorophore by the presence of the target analyte. Experiments have shown success using a single microscope object to deliver the focused laser light as well as collect the emitted fluorescence. The detection limit was reported [77] at 1 ppm while separating a mixture of 10 explosive related compounds (ERCs) in under 60 seconds. Lastly, lab-on-a-chip devices have demonstrated detection of explosive analytes by optical absorbance. Lack of depth in microchannels limit the effective sensitivity for such devices although work [77] has shown increasing channel depth to ~100 microns can happen without experiencing detrimental Joule heating. For a mixture of 13 different explosives, only TNT, TNB, and tetryl had detection limits less than 10 ppm.

Conclusions: Lab-on-a-chip devices offer advantages for deployable sensors including low power, high degree of integration, minimal consumables and waste, low cost, and efficiency. Detection limits reported to date would need to be improved. Acquisition of vapor or particle sample followed by salvation into solution prior to analysis may slow response time. Due to the versatility or sensing mechanism, it is envisioned lab-on-a-chip devices could sense a full range of substances. More development is needed to evaluate full potential of this sensing platform.

6.3.10 Organic thin film transistors (OTFTs). OTFTs have recently shown success at detecting solvent vapors as reported by Roberts et al [75]. Low-voltage transistor operation has attracted interest for low-power vapor sensing applications as well as operation in aqueous media. They have basic advantages of compatibility with flexible, large-area substrates, the properties of organic materials are highly tunable for chemical sensitivity and easily modified with receptor sites for specific interactions. The ability to control the film morphology provides yet another degree of versatility, directly influencing the pathway for analyte molecules to the transistor-critical semiconductor–dielectric interface. Notable advances include the incorporation of ultrathin, cross-linked polymer gate dielectric layers, such as divinyltetramethyldisiloxane-bis(benzocyclobutene) (BCB) or poly(4-vinylphenol) (PVP) cross-linked with

Trichlorosilanes reported by Roberts et al [75]. Self-assembled monolayer and multilayer dielectrics have also been used to achieve low-voltage operation and low-power complimentary circuits. These, among other methods of achieving low-power operation, could potentially be useful in OTFT sensor devices. Roberts et al demonstrated robust, high-performance OTFTs that are capable of detecting parts per billion (ppb) analyte concentrations in water, they have overcome a substantial hurdle for the realization of cheap and mass-produced aqueous sensors. They concluded the sensing mechanism (for both aqueous and vapor systems) involves small analyte molecules or ions that diffuse to the semiconductor–dielectric interface through grain boundaries within the film and influence the charge transport in the active layer.

In another study Roberts et al [74] discussed the stability of various organic semiconductors toward water and investigated the basic material requirements. The influence of molecular structure and side chain length on the stability in water was shown for Fluorene-thiophene oligomers (FTTF, DDFTTF) and multiple derivatives. Furthermore, they showed the influence of water on OTFT characteristics with different morphologies and thicknesses. The OTFT response was correlated with film morphology and thickness. Response from rough, nanocrystalline three-dimensional films to TNT was much greater than their two-dimensional counterparts. This work shows that trace chemicals can be electronically detected using organic transistors in water. [74]

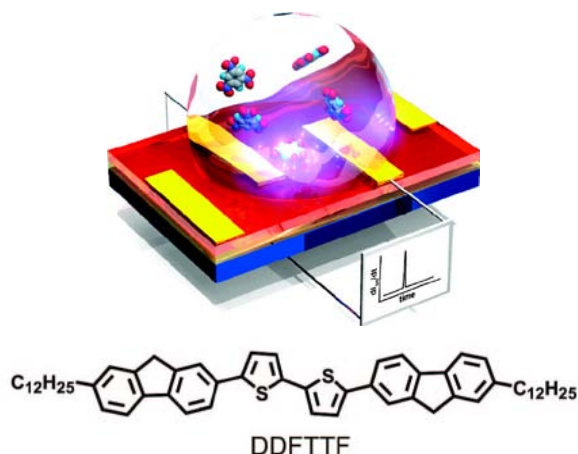


Figure 20: Animation of OTFT with TNT in aqueous solution (above) and derivative of fluorine-thiophene (below) used as the red surface layer. [74]

Roberts et al [74] also investigated another important challenge facing organic transistor based sensors is the ability to discriminate between various analytes. While a few examples have been reported showing an increased sensitivity to a particular analyte by imparting functionality to the semiconductor layer, the fundamental explanation describing the change in current in response to a particular analyte is lacking. Strategies to achieve specificity could be as straightforward as incorporating a sensor layer with enhanced specificity toward a particular analyte or integrating a selective membrane on the surface of the OTFT to eliminate exposure to non-target analytes. Their current studies are focused on investigating such methods to achieve specificity using molecular and interface engineering. The influence of film morphology on sensor response time and sensitivity demonstrated detection of a 40 ppm solution of TNT. They did not attempt to

detect lower concentrations of TNT although they previously reported [74] as low as 300 ppb for 2,4,6-trinitrobenzene (TNB). The OTFT sensor characteristics for TNT vary from typical sensor response curves, where a change in current is observed followed by saturation to a constant value. However, most sensor characteristics reported to date have been performed in the vapor phase rather than in a complex background, such as water. While the mechanism for the current change is not completely understood, the difference in response for films with different grain sizes exemplifies the importance of grain boundaries and diffusion and adsorption at these critical interfaces. In addition, chemical exposure to the interface of the electrodes may be highly variable causing device inconsistencies.

Conclusion: It is clear OTFTs have attributes consistent with low-power, small size sensor platforms. The work described here show effectiveness in aqueous as well as vapor backgrounds, which may add robustness being able to handle real world conditions. In addition, it is plausible to envision sensor arrays to improve selectivity and discrimination from background signals. It is not clear if these platforms will be sensitive enough for explosive specific detection due to the number of molecules needed at the grain boundaries to influence sensor response.

6.3.11 Micro-ring resonators. Micro-ring resonators are incorporated in a broad range of optical devices, including wavelength filters, wavelength division multiplexers and demultiplexers, lasers, switches, modulators, dispersion compensators and polarization rotators. Micro-ring resonators are also a good platform of miniature optical sensors to measure temperature, strain and stress, and to detect chemical and biological agents as reported by Chen [25]. They are capable of high Q-factor and long photon life-time, which enhance sensor response. The small size of micro-ring resonators also requires smaller amount of analytes for bio- and chemical sensing typically several micrometers to a few hundred micrometers in size. This unique advantage makes micro-ring resonators ideal for large-scale integration to form an array of sensors on a single chip. It also makes them highly suitable for monolithic integration with silicon integrated circuits that interface with the sensors. [25]

Chen also reported the different materials used to fabricate micro-ring resonators, although focused on polymer based materials due to their flexibility of processing, optical tunability, and other sensing properties. Tailored properties such as index of refraction, birefringence, absorption spectrum, etc are an important feature of polymer-based micro-ring resonator device design. They can be fabricated by photolithography and reactive ion etching, imprinting, soft-lithography molding, two photon polymerization, and electron-beam (e-beam) writing. Polymer optical waveguides can also be fabricated on flexible, curved, and conformal substrates. These advantages allow polymer micro-ring resonators to have functionality, performance, design, and fabrication flexibilities not available in other materials. [25]

Chen recently reported [25] on the use of chromophores with micro-ring resonators. Chromophores are molecules or functional groups as part of a larger molecule that have a distinct color based on characteristic absorption bands in the optical wavelengths. If

chromophores are randomly oriented in the polymer matrix, the polymer can have strong nonlinear optic effects, two-photon absorption and fluorescence, and sensitivity to chemical analytes. Specific chromophores structures can have a strong dipole moment and can be preferentially orientated through electrical or optical poling. The poled polymers become electro-optic materials and highly electronegative chemicals, such as nitroaromatic explosives TNT, DNT, etc., have shown strong interaction with conjugated charge transfer chromophores and thus change the optical properties of chromophore-doped polymers. This makes such polymers useful in detecting trace explosives. Exposure to ultraviolet (UV) and energetic electron beam permanently reduces the index of refraction of the polymer, which can be used to fabricate optical waveguides and micro-ring resonators.

By combining chromophore-doped polymers with optical resonator structures such as waveguide micro-ring resonators and fiber Bragg gratings, a variety of sensors can be made. Chen reported specifically on a compact explosive sensor based on micro-resonators made in chromophore doped polymers by photobleaching. The chromophores can be randomly oriented in the polymer matrix. He observed when a polymer that contains second-order nonlinear optical chromophores and they are preferentially oriented, the polymer exhibits macroscopic second order nonlinear optical properties and becomes an electro-optic polymer, and the polymer can be used for electro-optic sensors. [25] He stated detection sensitivity of DNT at ppb level with good specificity has been demonstrated, and the polymer has the potential of pushing the detection limit to the ppt level. Chen concluded that new polymers with more desirable sensing properties will continue to emerge as molecular design and organic synthesis continue to advance, enabling better sensors and new applications.

Sun et al [71] reported on detailed analysis of the chemical vapor sensing performance of two important ring resonator configurations where a vapor sensitive polymer layer is coated on the exterior or interior surface of the ring resonator, as shown in the Figure 21 below.

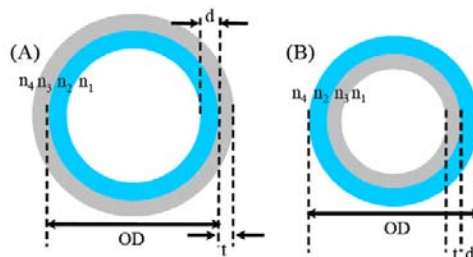


Figure 21: Ring resonator with polymer layer on the exterior (A) or interior (B) surface. t = polymer thickness. d = ring resonator wall thickness. n_1 , n_2 , n_3 , and n_4 are the refractive indices for the medium inside (air), silica ring resonator, polymer, and medium outside (air), respectively. [71]

Sun et al [71] observed the effectiveness of each configuration and concluded the following:

- When the polymer is coated on the outer surface the polymer layer of both low and high refractive index supports a potential well. When the polymer is coated on the inner surface, the polymer mode can form only with the high refractive index polymer.

- The refractive index sensitivity depends on the mode order.
- While in the outside coating case, the sensitivity does not depend heavily on the ring resonator wall thickness, the ring resonator wall plays an important role in the inner coating case.
- Thickness sensitivity studies show that the wave guide mode (WGM) shifts to a longer wavelength when the polymer layer expands.
- Using the simulation results and the typical values for many vapor molecules, they found this ring resonator chemical vapor sensor is capable of detecting a vapor concentration on the order of 100 ppb.

In a different study, Sun et al [69] also reported on the development of a rapid vapor sensor using an optofluidic ring resonator (OFRR) that naturally integrates the ring resonator with microfluidics, as shown in Figure 22 below. Rather than using the outer surface for sensing, the OFRR utilizes the optical field in the polymer layer coated on its inner surface. Analyte and mixing gas is pulled through the capillary while excited from the exterior. A thin wall is necessary to ensure sufficient light exposure in the polymer.

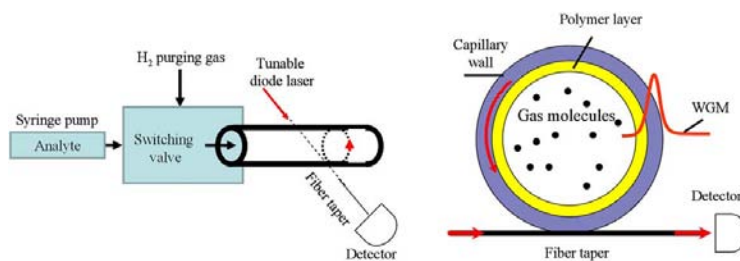


Figure 22: Flow diagram and cross-section view of an Optofluidic ring resonator (OFRR). [69]

There are a few advantages with this type of ring resonator as a vapor sensor. First, the OFRR relies on the excellent microfluidics of a capillary, which results in rapid response time and extremely low sample volume. Second, detection can be performed at any location along the capillary. Therefore various polymers can be patterned along the capillary and respond differently to different analytes, thus enhancing the vapor detection selectivity. And lastly, the OFRR is highly compatible with gas chromatography (GC) which can be explored for micro-GC development. [69]

Conclusion: Various ranges of sensitivity of this sensor platform have been reported although it is directly related to the materials coated onto the micro-ring resonator. It is possible to envision a highly selective sensor array with multiple polymers coating multiple resonators. Optical based excitation and microfluidic adaptation are two strong attributes of this sensing platform. It seems evident more efforts are needed to mature this technology before applications can be realized.

6.3.12 Fabry perot gas sensor. Liu et al [70] reported recently on the development of a Fabry-Perot (FP) cavity gas sensor. They argue it is highly desirable that the FP cavity is able to accommodate various polymers that may have wide ranging refractive index. It is widely argued different polymers respond differently to vapor analytes and it is very common for a gas sensor to incorporate a matrix of polymers to enhance the vapor detection specificity. The FP cavity performance degrades tremendously when the

sensing material refractive index approaches that of the fiber, resulting in nearly indiscernible interference fringes, which limits the selection of the polymers. Liu was able to develop an easily-fabricated fiber-based FP gas sensing probe that can accommodate any polymer regardless of their refractive index, as shown below in Figure 23. It is composed of two layers: a silver layer and a vapor-sensitive polymer layer. Light propagating in a single mode fiber will be partially reflected at the silver layer and the polymer-air interface. These two reflected beams generate interference spectrum, although surface defects at the sensing material-vapor interface may reduce overall reflectance. As vapor of interest is introduced, the vapor-sensitive polymer layer will interact with analyte, and the change of its refractive index or thickness will change the light path, which in turn causes the interference spectrum to shift. By introducing the reflective silver layer, they are able to coat a polymer of any refractive index, thus tailoring the sensor platform for specific sensing materials. In their experiment, Liu was able to operate in continuous gas flow or pulsed mode to demonstrate the feasibility of the proposed FP gas sensor. [70]

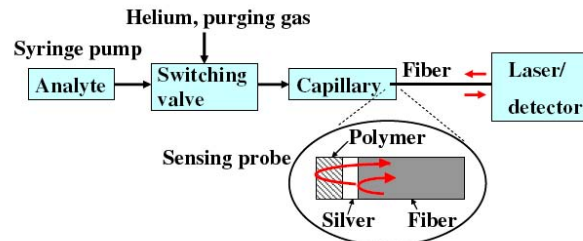


Figure 23: Diagram of Fabry-Perot gas sensor. [70]

The work determined sensitivity for methanol vapor with the detection limit of 1 ppm and 10 ppm, for two different polymers, respectively. In addition, they concluded future work would focus on optimizing the performance of the FP gas sensor by increasing the Q-factor of the FP cavity to improve the sensor spectral resolution and hence the detection limit, miniaturizing the sensing probe, and improving the fluidics to achieve faster detection in the continuous flow mode. [70]

Conclusion: The FP sensor offers a straight forward approach to use interference spectrums from reflection of light propagating through layers of sensory materials. This approach uses small, low-power components and is designed to be a very versatile sensor platform. The sensitivity of this sensor will be mostly affected by the thickness of sensing layer and morphology of the sensing layer. It is unclear how this platform addresses reversibility once analyte of interest interacts with sensing layer.

6.3.13 Nanofibrous membranes. Kumar et al [21] reported on an inexpensive and simple approach for the fabrication of high surface area sensing elements using electrospinning. This procedure allows exceptionally high surface area, opening new possibilities for the use of appropriate chemistry to tailor their surface properties and consequently using them for sensing applications. By applying a large static electrical charge to a polymer solution, extremely fine nanostructures (polymer fibers) are produced. Electrospun fibers are typically less than half a micron in diameter and can be

as small as 10 nm in diameter. With this geometry, they can have surface areas approximately 1 to 2 orders of magnitude higher than those of continuous thin films. In addition, functionalization, or mixing in additives to the polymer solution, of the electrospun fiber surface further provides possibilities in designing the sensing surface for various intended applications. The sensor platform, nanofibrous membranes, could be used as chemiresistors as well as fluorescence quenching sensors depending on the receptor used. For chemiresistor type sensors, conducting polymer nanotubes have been fabricated by combining electrospinning and vapor deposition polymerization, as shown in Figure 24 below. For an optical response, fluorescent dyes functionalize the surface of the nanofibers.

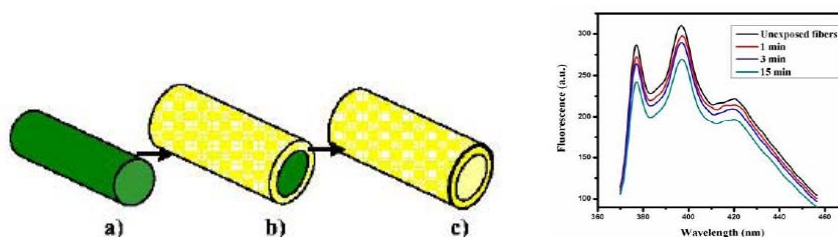


Figure 24: Depiction (left) of nanofiber (a) with conducting polymer coated nanofiber (b) and conducting polymer nanotubes (c) after the nanofiber has been washed away. Fluorescence spectrum over time showing continual quenching of functionalized polymer fibers. [21]

Kumar [21] concluded this method could be utilized for high surface area vapor sensing. The ability to functionalize fibers allows for enhanced selective sensing. Electrospinning has been used as an inexpensive technique for the fabrication of nanofibers. The approach developed in this study is generic and can be extended to other conjugated polymers as well. They were able to demonstrate fluorescence quenching detecting of trace amounts of DNT sublimating off a 2 milligram solid sample of DNT.

Conclusion: The method of electrospinning may offer a means of increasing surface area interaction between sensory materials and collected sample. Some advantages include; functionalized versatility, inexpensive, and optical or electrical transduction methods. It is unclear from this work how sensitive this mechanism could be although high selectivity could be envisioned. More work would need to be performed before recommendation for specific Army applications.

6.3.14 Surface enhanced Raman Spectroscopy (SERS). Over the past few years there have been applications of SERS as a sensor platform to detect vapor phase explosive molecules. Nobel metal nanoparticles or nanostructures have been observed to cause large enhancements of the Raman signals for adsorbed molecules through a combination of localized surface plasmon resonance and induced increases in molecular bond polarizability. Baker et al [89] reviewed several efforts focused on SERS enhancement and concluded the precise physics of this effect are under dispute, because experiments indicate there may be more than one enhancement mechanism. The two effects identified are an electromagnetic field enhancement via localized optical fields of the metallic nanostructures and a chemical or electronic enhancement (first layer effect) because of increases in Raman cross-section in contact with a metal nanostructure. Moore [31] also

reviewed more recent research efforts including one using electrochemically roughened gold and silver substrates to detect the TNT vapor with volumetric flow rates up to 0.4 liters per second. These SERS methods rely on accumulation of the analyte from the vapor onto the substrate, implying minute range analysis times when diffusion controlled, or faster if active air movement schemes are utilized. There are other efforts to incorporate resonance Raman enhancement with the surface enhancement, or surface enhanced resonance Raman scattering (SERRS). The development of SERS chips with unique polymer coatings that are selectively sorb ERCs is a current major research focus. In addition SERRS platforms have been incorporated with microfluidic devices and also demonstrated the use of SERRS 20 meters from the excitation source.

Conclusion: The use of Raman scattering as an analytical technique is currently in fieldable devices, although it suffers from lack of sensitivity due to extremely small cross-sections for ERCs. With the addition of surface and resonance enhancement, SERRS provides a means to utilize the highly selective Raman spectral features in an environment where the target materials are scarce. If sensitivity of this platform can be demonstrated in field conditions, then this technique may have many uses for Army applications. Reversibility of these chips was not clearly discussed in the literature.

6.3.15 Self powered sensors. Efforts in current sensor research have used selective polymers for more sensitive explosive detection via fluorescent chemosensors. Germain et al [55] focused on the use of a mitochondria-catalyzed biofuel cell for explosive sensing. The biofuel cell contains two electrodes: a cathode that will reduce oxygen to water and a bioanode that will oxidize pyruvate in a fuel container to carbon dioxide and water. The sensing mechanism is based on the unique ability of mitochondria on the bioanode to attenuate their ability to oxidize the pyruvate substrate/fuel and produce current in the presence or absence of nitroaromatic explosives, as shown below in Figure 25. Bioelectrocatalysis would be beneficial, because it combines the advantages of low cost, simplicity, and ability to detect small quantities. [55]

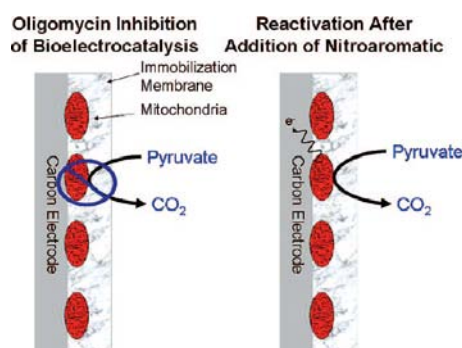


Figure 25: Sensing mechanism illustrating a nitroaromatic decoupling of a mitochondria-modified electrode. [55]

Germain et al [55] observed interesting responses when concentration studies were done, it was found that this type of sensor is not a quantitative sensor, but a threshold sensor which is either on or off, but whose signal does not change with concentration. Since the power response is a function of surface concentration of active mitochondria (similar to

enzyme systems), they concluded improving immobilization and inhibition methods would improve sensitivity. [55]

Conclusion: This sensing mechanism offers a unique method to detect the presence of nitroaromatics in solution phase. This method needs to function with a fuel solution, therefore sample handling processes may be complex. It is plausible to envision this as a potential compliment to lab-on-a-chip device along with microfluidic sample processing. The maturity of this type of sensor is clearly in the early stages. Sample handling may be the largest hurdle with this sensing mechanism and platform.

6.3.16 Porous silicon microcavity. Levitsky et al [38] reported on a chemosensitive polymer entrapped in porous silicon microcavity (PSi MC) containing entrapped polymer that allows detection of vapors of explosive nitroaromatics. The sensing mechanism is based on modulation in both fluorescence and reflectance signals. The FP cavity is fabricated between two distributed Bragg reflectors (DBRs). The MC resonant peak in the reflectance spectra is shifted upon vapor exposure. They observed broad polymer fluorescence showing patterning by the narrow MC peak, which is also sensitive to the vapor exposure. Such spectral patterning provides an additional parameter for recognition, namely, the dependence of fluorescence quenching on the detection wavelength. With most conventional fluorescence-based chemosensors employing flat substrates, it is not possible to display these spectral features. As a result, their fluorescence quenching exhibits no wavelength dependence. [38] Levitsky concluded PSi microcavities filled with conjugated emissive polymers can be used as chemical sensors to detect nitroaromatic explosives with low vapor pressures. The unique aspect of this sensor platform involves these sensors working simultaneously in reflective and in fluorescence regimes. This scheme allows the introduction of an additional set of parameters (detection wavelengths) to uniquely characterize specific explosive vapors and potential interferents.[38]

Conclusion: This sensing platform offers unique attributes namely, wavelength dependent fluorescence. In addition, a sensor array could be designed with different sensory polymers entrapped in microcavity or one polymer entrapped into spatially distributed microcavity. Although sensitivity of this approach will depend of the polymer chosen, the potential sensitivity is unclear. Fabrication of these devices seems inexpensive, although it isn't clear how reversible this method could be once the polymer interactions with the target analyte. If reversibility could be solved, this may have potential uses for Army applications.

6.4 Novel Sensory materials

The following descriptions will overview nascent and novel materials and methods that may preferentially sense the presence of ERCs. With the combination of the sensing platforms discussion, a more complete sensing system can begin to be envisioned. This is not meant to be a complete list since there were time constraints to this work.

6.4.1 Pentiptycene gas sensors. Zyryanov et al [42] reported on multiple variations of pentiptycene-based molecules and their response to TNT and DNT. They observed that the sensor films show a different degree of quenching for each vapor analyte. The fluorescence of the sensor films was largely restored when the films were washed by a stream of clean air, demonstrating good reversibility. This suggests that these easy-to-make sensor films may be used in array-based sensors for nitroaromatics. [42]

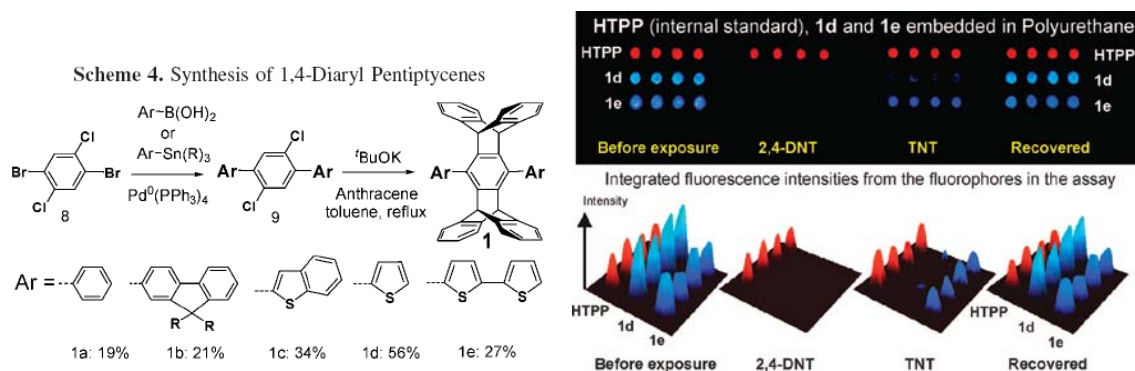


Figure 26: Five variations (left) for the synthesis of 1,4-Diaryl Pentiptycene. (Right Top) Photograph of the sensor slide before and after exposure to DNT and TNT in their equilibrium vapors at 22 °C, and recovery in clean air stream. (Right Bottom) Integrated light output from corresponding photograph allowing signal quantification. [42]

They observed that developing a simple method for synthesis of 1,4-diarylptentiptycenes, the respective yields were moderate considering that four consecutive steps are involved (20-56% overall for four steps, i.e., 60-85% per step). The preliminary fluorescence quenching experiments resulted in the evaluation of DNT and TNT interactions at 180 ppb and 7.7 ppb equilibrium vapor concentrations, respectively. The variations of 1d and 1e (left image on Figure 26) showed a high degree of fluorescence quenching compared to the other variants. They concluded these observations suggest that 1,4-diarylptentiptycenes could be of potential interest for the fabrication of sensors for explosives. [42]

Conclusion: While this study does not perform detection limit studies, it is clear these pentiptycene variants produce response for equilibrium vapor TNT, although not DNT. There are multiple platforms that could be envisioned with this sensory material, although only as a targeted TNT vapor sensor. Good reversibility is evident for Figure 26 showing a return of fluorescence.

6.4.2 Multiphoton fluorescent quenching. Narayanan et al [66] investigated the use of amplified sensing polymers. Their several advantages are derived from the ability to synthetically tailor these materials to a required resonance energy, solubility, and even chemical selectivity for particular applications. One major attribute of the three-dimensional iptycene structures (shown in Figure 27) involves the ability to isolate the polymer backbones of P1 and P2 and thereby reduce intermolecular electron/orbital coupling and self-quenching that usually accompanies these interactions. Using nonlinear optical probes, multiphoton excitation of these systems may provide additional selectivity. They claim using a multiphoton excitation sensing scheme allows one to

move out of the visible excitation regime (excitation can be in the near-IR and beyond). They performed multiphoton absorption measurements in two amplified sensing polymers using infrared excitation. The polymers display large two-photon absorption cross sections, and their bright multiphoton excited fluorescence is sensitive to the presence of TNT. They also performed two-photon and three-photon excited fluorescence quenching measurements in the presence of TNT, which was larger for P2. [66]

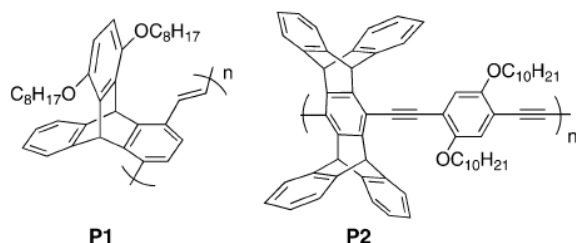


Figure 27: Two variations of iptycenes investigated by Narayanan et al [66].

They concluded multiphoton excited fluorescence quenching measurements offers several advantages for sensitive detection in the IR spectral regions in order to allow for eye safety for standoff sensing applications. Synthetic modifications based on known structure-function relationships may provide further enhancement of the two-photon absorption cross-section. [66] The development of such polymers as multiphoton sensors with controlled properties may offer a new avenue for improved selectivity.

Conclusion: These sensory materials offer two fold enhancement; an increased quenching factor after multiphoton excitation improving sensitivity and the ability to move the excitation source in the IR where more eye safe applications are possible and sources are more mature and inexpensive. These materials also offer solutions for both remote and standoff applications. Clearly, more experiments are needed with complex mixtures and potential interferents as would be experienced in real world conditions.

6.4.3 Turn-on fluorescence. Andrew et al [67] investigated sensory materials inspired by enzymatic reduction of RDX in contaminated wastewater. They sought to mimic this biological process in a fluorescence-based sensor. Initial studies targeted 10-methyl-9,10-dihydroacridine (AcrH₂) because of its ability to form the fluorophore (AcrH⁺) upon loss of H⁺. The chemical structure is shown below in Figure 28. They observed results where both RDX and PETN generate a shifted emission from AcrH⁺ upon photolysis excited at 313 nm in acetonitrile solutions. Other chemicals such as TNT showed very little effect. Utility of this material was considered impractical due to oxidation, however, a zinc analogue was synthesized to improve the photostability. [67] They concluded that AcrH₂ is capable of selectively transferring a hydride ion equivalent to saturated nitramine and nitrate ester explosives as part of a photochemical reaction. In addition they determined the photostable zinc analogue displays an 80- and 25-fold increase in 480 nm emission intensity upon reaction with RDX and PETN, respectively. [67]

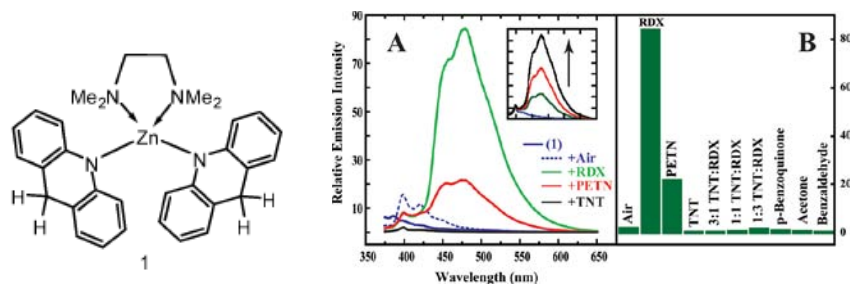


Figure 28: Molecular structure (left) of 10-methyl-9,10-dihydroacridine (AcrH₂) (zinc analogue). Interactions of AcrH₂ (right including emission profiles (A) as well as emission intensities (B) mixed with explosives and excited using a 313 nm source. [67]

Conclusion: This work shows capability of using direct fluorescence response to detect RDX and PETN although the sensory materials would need to withstand vapor sensing applications. The maturity of this technique would need to be improved and tested to properly evaluate its effectiveness. There are multiple sensing platforms that may be compatible with this material. The solution-based experiments showed very high selectivity toward RDX and PETN, which would compliment other nitroaromatic based sensors. Army applications would benefit greatly from this capability.

6.4.4 Biomimetic coatings. Jaworski et al [63] recently reported on materials that mimic biology. Currently, many sensors rely on pattern recognition of nonspecific sensors to distinguish molecular species, although the affinity differences are often insufficient for highly selective and sensitive chemical analysis in realistic conditions. They were able to exploit an evolutionary screening process to identify highly selective peptide-based recognition of TNT and DNT and develop gas-phase binding assays that can be selective prototypes. They demonstrated increased selectivity results from multivalent binding after mutating the peptide sequences. In addition they showed the ability to immobilize the DNT binding peptide with ethylene glycol oligomers. With this configuration they were able to selectively detect gas-phase DNT molecules in mixtures containing TNT. [63]

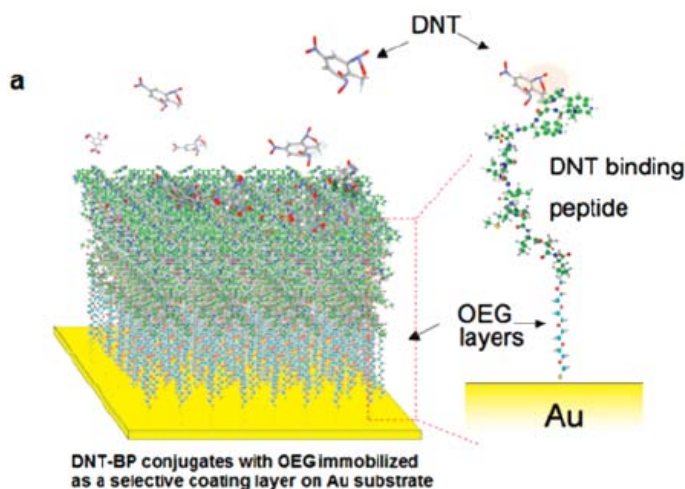


Figure 29: Animation of DNT vapor molecules undergoing multivalent binding to peptides that are anchored to gold substrates by ethylene glycol oligomers. [63]

They identified specific TNT and DNT binding peptides through an evolutionary screening process. Peptide chains consisting of tryptophan, histidine, imidazole, etc were formulated. For example, they stated tryptophan's interaction with TNT may take on a donor-acceptor character due to the electron deficiency of the ring in TNT, while those of tryptophan are electron rich. Imidazole side chains may coordinate with the nitro group in the TNT molecules through partial charge-charge interactions or hydrogen bonding. [63] They concluded that successful evolutionary screening discovered highly selective peptide receptors, which coincide with the TNT binding sites. Using mutational analysis, they demonstrated that multivalent binding is the key to selectivity of the TNT binding motif. In order to make the discoveries relevant for gas-phase chemical sensing, they created a biomimetic coating for highly selective detection of DNT in ambient conditions. They believe that this approach of evolutionary peptide screening followed by the creation of biomimetic coatings reflects a significant advance to enable highly selective and sensitive miniaturized chemical sensors. [63] In a separate study, Cerruti et al [64] developed a sensing coating for detecting explosive molecules in water by embedding peptide based receptors with high affinity for explosives molecules such as TNT and DNT, into a polymeric matrix. [64]

Conclusion: Peptide based multivalent sensing materials detect desired molecules in a highly selective manner. Multivalent binding utilizes many intermolecular attractions such as, van der Waals and hydrogen bonding, results in stronger overall binding. It isn't clear if these materials are reversible. It is possible these materials could truly enhance discrimination from background interferents although more studies would be needed. Sensitivity as well as detection limits were not the focus of the study, which would also need to be determined. Using a gold substrate may limit compatibility with some sensor platforms, although it may be possible to use other substrate materials. Many Army applications would benefit from this capability.

6.4.5 Cyclodextrin-based molecularly imprinted polymers (MIPs). Ju et al [65] investigated improvements in sensitivity and selectivity by combining molecular imprinting and receptor effects. Receptor molecules, such as cyclodextrins (CDs), are effective for the incorporation of nitro-aromatic compounds. They were able to use a molecular template to create a selective sensing surface, which revealed higher selectivity towards 2,4-DNT and 1,3-dinitrobenzene (1,3-DNB), while lesser responses are observed with other structurally-related guest molecules. They also observed when TNT penetrated into the cavity of cyclic CD, it would not bind efficiently. They concluded this indicates the sensitivity and selectivity towards 2,4-DNT was created by a synergic effect of the host-guest interaction with the cyclic CD molecule and the presence of the imprinted cavity. They reported detection limits for 2,4-DNT at sub-ppb concentrations in solution. [65]

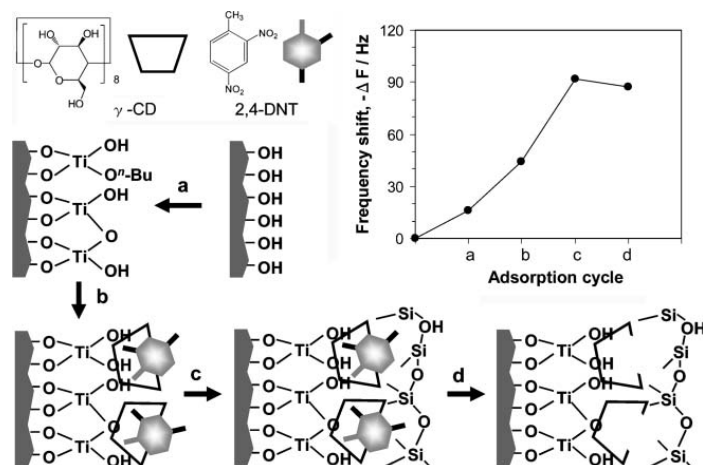


Figure 30: A step-wise construction of the CD molecularly imprinted surface (follow the arrows). [65]

Conclusion: Since all the reported data was solution-based further examination of the sensor response in open air and in realistic environments is needed. In addition, robustness for such a complicated surface structure would need to be studied. Relaxation of imprinted “hole” may also cause sensitivity to diminish over time. More potential interferents would need to be investigated. Further maturity is needed before a thorough evaluation can occur.

6.4.6 Pyrrole receptors. Stepien et al [78] recently sought to produce a liquid crystalline mesophase based on an all-carbon-linked, aromatic expanded porphyrin framework. They reported on the synthesis of new cyclopyrrole derivatives (shown in Figure 31 below) that form a mesophase hexagonal column when combined with electron-deficient acceptors, such as trinitrofluorenone (TNF), trinitrophenol (TNP), TNB and TNT. For sensing purposes, the possibility of producing liquid crystalline structure upon exposure to TNT makes the new cyclopyrroles a potential explosives-sensing material. [78]

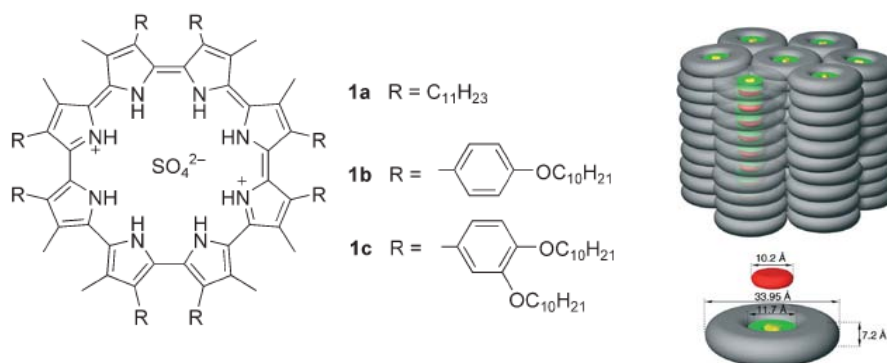


Figure 31: Molecular structure of cyclopyrroles 1a-c (left) with a hydrogen bonded sulfate ion. Idealized packing (right) of the liquid crystalline phase (look like innertubes) of 1c. The red molecules are TNB.

Stepien et al [78] stated that the self-organization of the cyclopyrrole hexagonal mesophase, which is induced by vapors of polynitroaromatic compounds, makes this a potential interesting sensing mechanism. They are aware this material may be impractical although the working principle demonstrated could be refined to provide new

complementary sensors. One key sensing property includes intense and extremely redshifted electronic absorptions (above 1100 nm in the case of cyclopyrrole) with a dramatic change in this region of the spectrum in the presence of TNT vapors, [78]

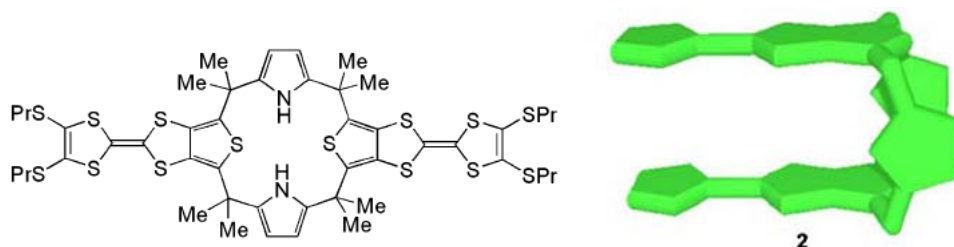


Figure 32: Molecular structure (left) of receptor, bis-tetrathiafulvalene (TTF)-calixthiophenepyrrole. Idealized 3-D depiction (right). [79]

In a very recent publication by Kim et al [79], a new receptor, the bis-tetrathiafulvalene (TTF)-calixthiophenepyrrole, was developed. This new system is found to form complexes with the electron-deficient guests, TNB and picric acid (PA), which serve as models for nitroaromatic explosives. The binding phenomenon occurs when the receptor forms a sandwich-like host (shown in Figure 32 above), which results in an easy-to-visualize color change in chloroform. Support for the proposed binding mode comes from a preliminary solid state structure of the complex formed from TNB. They reported color changes observed when dichloromethane solutions of the receptor are added to solvent-free samples of TNB, PA, and TNT supported on silica gel. [79]

Conclusion: Although Stepien et al claim the sensory material is impractical, it did respond to explosive vapors within one second of exposure. They investigated similar structured nitroaromatic compounds, although it is not clear if these porphyrin-based sensors can discriminate from interferents. It is not clear if these materials are reversible. The receptor reported by Kim et al was more designed for colorimetric-based “naked eye” color change sensing. Reversibility is also a challenge for these materials. More investigations are needed in order to evaluate properly. Rapid, inexpensive, colorimetric-based sensing may provide some solutions to Army applications, although needing a sample in solution-phase limits many applications.

6.4.7 Fluorescent nanofibril sensors. Naddo et al [73] reported an efficient sensing film fabricated from the alkoxycarbonyl-substituted, carbazole-cornered, arylene-ethynylene tetracycle (ACTC), shown in Figure 33 below. One advantage of this material includes carbazole, which enhances the electron donating power of the molecule and thus increases the efficiency of fluorescence quenching by oxidative explosives. In addition, the large-area planar molecular surface of ACTC enables effective long-range orbital (π - π) stacking between the molecules via nanofiber fabrication. Previous research has demonstrated that one-dimensional π - π stacking is highly favorable for electron-hole pair, or exciton, migration. They stated the ACTC structure would promote long-range exciton diffusion, which promotes enhanced sensitivity. In addition, the robust molecular structure of ACTC, within the networks of nanofibers, produces high surface area porosity, which makes it ideal for sensing oxidative gaseous molecules. They observed

Figure 1 consists of two panels. The left panel shows the chemical structure of the DNT molecule, which is a bis-indole derivative with a long alkyl chain (R) attached to the nitrogen atoms. The right panel shows the photophysical properties of the DNT molecule. The top graph shows the absorption and emission spectra of the pristine film and the quenching of the emission by DNT and TNT over time. The bottom graph shows the quenching of the emission by DNT and TNT over time.

Chemical Structure: The chemical structure of the DNT molecule is shown on the left. It consists of two indole rings linked by a methylene group, with a long alkyl chain (R) attached to the nitrogen atoms. The structure is shown in a 3D representation with a blue background.

Photophysical Properties: The right panel shows the photophysical properties of the DNT molecule. The top graph shows the absorption and emission spectra of the pristine film and the quenching of the emission by DNT and TNT over time. The bottom graph shows the quenching of the emission by DNT and TNT over time.

Intensity vs. Wavelength: The top graph shows the intensity of the emission spectra as a function of wavelength (nm). The x-axis ranges from 350 to 550 nm, and the y-axis ranges from 0 to 800. The curves show the emission spectra of the pristine film (black), 10 s (red), 20 s (green), and 60 s (blue). The intensity decreases as the exposure time increases.

Quenching (%) vs. Exposure time: The bottom graph shows the quenching percentage as a function of exposure time (s). The x-axis ranges from 0 to 60 s, and the y-axis ranges from 0 to 100%. The curves show the quenching of the emission by DNT (black squares) and TNT (red triangles) over time.

Other observations included faster quenching by DNT upon exposure mostly due to the increased vapor concentration of DNT versus TNT. In contrast, the total percent quench over time was nearly equivalent due most likely to increased partitioning of TNT into the film. Since the emission wavelength of ACTC is far above the absorption range of the two explosives, there is no possibility for excited state energy transfer. Therefore, the observed fluorescence quenching must explicitly be due to the photoinduced electron transfer from the excited ACTC to the quencher. [73] They observed efficient quenching for the sensing film over repeated use, implying high stability of the film against photobleaching. They concluded a new type of fluorescence sensory material has been developed most likely due to the extended 1-dimensional molecular stacking between the component molecules (favoring exciton migration) and intrinsic nanoporous morphology (favoring diffusion of vapors) formed within the film. In addition, reversibility studies showed a slow recovery after a few days with air or a much faster recovery to nearly 90% upon exposure to hydrazine for one hour. [73]

6.4.8 Pyrene quenching assay. Hughes et al [23] recently reported on a powerful and relatively inexpensive sensor design for nitrated organic explosives. They utilized the well known ability of these analytes to quench pyrene fluorescence and parlayed it into an assay of quenching fluorophores in aqueous solutions. They created varying concentrations of pyrene, pyrene excimer, a pyrene–perylene fluorescence resonance energy transfer (FRET) pair, and a diphenylanthracene (DPA) and embedded pyrene in

hydrophobic micelles within the solution. They claim the use of micelles would assist sensitivity, promote differential quenching as a feature for pattern recognition, and protect pyrene quenching from molecular oxygen. [23] Combining these fluorophore solutions in an array, and examining the fluorescence over two bandwidths resulted in a “fingerprint” for each analyte that allowed it to be classified according to its molecular identity using linear discriminant analysis (LDA). They observed good sensitivity and selectivity with explosive compounds including TNT, RDX, HMX, Tetryl, and nitrobenzene. They concluded that the modular nature of this array means that it is expandable as alternative surfactants and fluorophores are considered. [23]

Conclusion: The fluorophore assay is a unique method of discriminating within explosive species as well as interferents. It may be challenging to envision the practical application of this type of sensor for field use, although lab-on-a-chip devices may be an appropriate sensing platform. These types of materials will only function in a solution due to pyrene quenching in presence of oxygen. The results show very good discrimination with LDA, which may be applicable to other sensor array development. More development is needed to properly evaluate this sensing material for field applications.

6.4.9 Photoluminescent particles. Luminescence is the process in which energy is emitted from a material at a longer wavelength than which it is absorbed. Photoluminescence includes fluorescence and phosphorescence. Fluorescence proceeds and ceases spontaneously as the excitation source is turned on or off. Phosphorescence persists up to microseconds after the excitation source is removed. These processes lead to time-resolved luminescence which is used to suppress background signatures. Using colorimetric based sensing, Alaoui [80] was able to show an increase in sensitivity detecting explosives tagged with europium (Eu^{3+}) complexes showing long lived luminescence. These luminescent particles were spotted on filter paper coated with different amounts of NG, RDX, and smokeless powders. When these explosives are analyzed from fingerprints left behind, time-resolved luminescent imaging suppresses unwanted background signals and leads to more effective detection. The photoluminescence detection of trace explosives showed superior sensitivity to current colorimetric methods found in Explosive Testing Kits. [80]

6.5 Standoff Sensing

The following descriptions focus on standoff sensor technologies. Recent interest has spurred a wide variety of development in this area. In contrast sensory materials, detection distance is a key evaluation factor, which corresponds to removal of the warfighter from blast radius of most explosive threats. Most techniques are based on optical or laser-based excitation.

6.5.1 Photothermal deflection spectroscopy (PDS). Recent work by Van Neste et al [14] utilizes bimaterial (Au and SiN_x) microcantilevers to detect changes in IR absorption. Their experimental setup included a one meter standoff target with approximately one microgram/ cm^2 of explosives TNT, RDX, and PETN. The cantilevers

were co-located with the IR source (2.5 μm – 14.5 μm). IR radiation was sent to the target and deflected back to a mirror, which focused the photons onto the SiN_x side of the microcantilever. As the target explosives absorb the IR radiation as a function of wavelength, the energy reflected to the cantilever detector is lowered resulting in a decrease in cantilever heating, or bending. The resulting inverted absorption peaks are therefore found at the wavelength corresponding to the peaks in molecular IR absorption of the target species.

For specific parts of the spectrum, peaks from symmetric and asymmetric stretching of NO_2 correlated to IR absorption spectra in the literature, however intensity of the peaks varied most likely due to surface effects. They achieved a sensitivity of 100 nanograms/ cm^2 by using a low power IR source at a distance of 1 m. The method has potential for very high sensitivity. Increasing IR power and improving geometric cantilever design, it may be possible to increase standoff distance. [14]

Conclusion: PDS offers a unique application of microcantilevers and could present a plausible solution for standoff sensing although non-reflective surfaces may limit sensitivity photons over distances longer than 1 meter. Since IR absorption is specific to functional groups of a molecule, this technique should have robust selectivity. For field applications, mechanical vibration interference may increase background noise of the cantilevers.

6.5.2 Differential reflectometry spectroscopy (DRS). Differential reflectometry involves modulation of the electronic structure of materials. As with most standoff explosive detection methods, this method relies on analyzing samples on surfaces. By measuring the normalized difference between reflectivities of two adjacent parts of the same specimen, it is possible to identify the ‘fingerprint’ of each material analyzed. Typically the excitation source ranges from the ultraviolet (UV) to the near infrared and reflected light is collected in a light sensitive detector. Taking the difference of the two measured reflectivities and dividing by the average reflectivity yields the desired normalized result. Measuring the reflectivities at the same time allows for reduction in spectral fluctuations created in the source, detector, or surface.

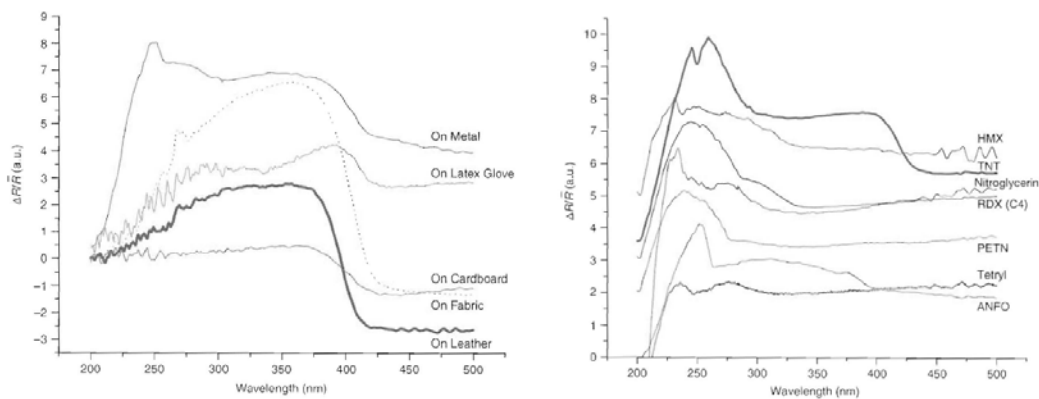


Figure 34: DRS plots (left) of TNT on various surfaces. DRS plots of various explosives (right) on same surface. [77]

Recent work by Hummel et al reported [77] limit of detection in laboratory setting was approximately 10 micrograms per square millimeter. It is unclear the standoff distance between the source/collection optics and the contaminated surface. With regard to solid material on substrate, it is clear that varying substrates may affect the deployment of this technique in the real world. The figure above shows response of TNT on various surfaces showing some repetition although substrate effects do exist. In addition, multiple explosives have been analyzed on the same substrate and show distinct spectral differences.

Conclusion: DRS is capable of producing discriminant spectra of many explosives in laboratory environments. Substrate effects from surfaces in real world conditions may increase background noise. This technique may have limited sensitivity with regard to the detection limits reported. In addition, the requirement of two specific reflectances from adjacent regions of a sample on a surface may lead to limited signal due to heterogeneity of real world surfaces.

6.5.3 Coherent Anti-stokes Raman (CARS). CARS is an evolving technique that may show relevance to standoff explosive sensing. This technique takes advantage of non-linear optical effects when two or more laser beams generate a third coherent beam shifted toward shorter wavelengths relative to the original beams. Changing the frequency of one originating beam can create spectra. In addition to potential for standoff detection, 3-D spatial resolution may be possible. Although limited amount of efforts have been published regarding explosive targets, CARS may have potential. The inherent weak Raman signal causing sensitivity issues will persist with CARS. [3]

6.5.4 Laser-Induced Breakdown Spectroscopy (LIBS). LIBS is a developing technology that may provide the capability to detect explosive residues at standoff distances. The concept involves focusing a short laser pulse in air or on a surface to create a “breakdown” or plasma. These plasmas are created in very small volumes depending on focal length as the energy density increases above a certain value for air. The plasma interacts and consumes substances on surfaces, dissociating them into ions, neutrals, electrons, and fragments. As these particles recombine they emit photons at specific wavelengths that can be correlated to specific elements. Most importantly, all elements emit photons within the spectrum of 200-980 nm. Spectral databases exist to provide identification capabilities. Selectivity problems arise due to the fact the base elements of explosives are very similar to those ubiquitous in the environment. Enhancements to selectivity have been proven by including a second pulse with a short interpulse delay (microseconds). This reduces atmospheric effects on the spectral response.

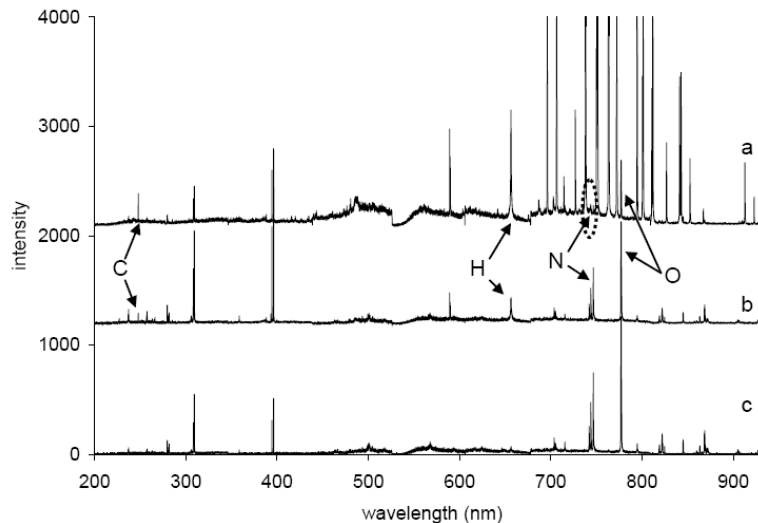


Figure 35: LIBS emission spectra of (a) RDX on aluminum under argon, (b) RDX on aluminum in ambient air, and (c) aluminum in ambient air. [88]

The subsequent emission can be resolved spectrally and temporally in order to generate a spectrum containing emission lines from the atomic, ionic, and molecular fragments created by the plasma. Typically, a laser is used to produce a pulse width of a few nanoseconds. This laser pulse is focused onto the sample surface. When the laser power at the focal point exceeds $\approx 1 \text{ GW/cm}^2$, a microplasma is created. [88] Emission from the microplasma is then collected by a series of lenses and delivered to a spectrometer in order to resolve the collected light. Finally, the spectrally resolved light arrives at a detector in order to generate a LIBS spectrum, as shown in Figure 35 above. [88] From the spectra it is possible to observe the difference when normal atmosphere is removed from the plasma. The ratios of emission line intensities for oxygen to nitrogen demonstrates the ability of LIBS to track relative amounts of elements in a sample. In most cases, the increase of oxygen relative to nitrogen above the typical 1:4 ratio indicates the presence of an energetic material. Due to optical excitation by laser, it is clear that LIBS has potential to

Conclusion: As previously mentioned, interference from atmospheric oxygen and nitrogen is a problem when trying to detect explosives. Given complex real world conditions, the plasma will also cause emission from the surface material an explosive rests on as well as any environmental contamination, such as dust, grease, oil. Double-pulse LIBS minimizes the contribution from the surrounding atmosphere. For the standoff application, eye safety is a major concern. One way to alleviate this problem is to use eye-safe laser wavelengths, such as $1.5 \mu\text{m}$. The laser power at the focus can still cause eye damage, but the majority of the laser path length and any reflections of the beam will be in the eye-safe region. [88] Other drawbacks are poor reproducibility and sensitivity. The irreproducible nature of plasmas causes differences in the laser coupling with the sample. While LIBS has been shown to be able to detect explosives residues, the limit of detection has not yet been established, namely due to the consumption of the sample during each plasma event. They are difficult to quantify, although most studies have concluded are around ppm. Advantages for LIBS include no sample preparation, no

waste or cost generated by consumables and a spectrum can be collected in real time. These attributes make LIBS very attractive for standoff detection of explosive residues on surfaces to assess possible threats.

6.5.5 Photo Fragmentation – Laser Induced Fluorescence (PF-LIF). PF-LIF is a technique that uses a UV laser pulse to fragment vapor phase explosive compounds producing NO-radicals. A second UV laser pulse further excites the NO-radical to a higher vibrational state causing fluorescence at a wavelength shorter than the original UV pulses creating unique spectra. Atmospheric NO containing compounds have only a fraction of NO existing at the respective vibrational state compared to explosive NO fragments. This technique may offer standoff detection capabilities although there is no selectivity within the nitro based family of compounds. In addition, sensitivity will be challenged by relying on vapor phase detection. Some researchers have been able to achieve ppb level sensitivity in laboratory conditions. [3] The two major advantages of this method include (1) the collected fluorescence was at lower wavelengths than the exciting laser, and (2) there was no fluorescence from the ground-state NO that is present naturally in air, thereby reduces the probability of a false alarm. Using relatively high laser energy (~5 mJ), a large interaction volume (unfocused laser), an improved detection system (with tailor-made spectral filters), and a background-free scheme, researchers demonstrated PF-LIF at 2.5 meters under near-ambient conditions (1 atm and 28 °C), with an detection limit less than 15 ppb. [88]

Conclusion: PF-LIF offers the ability to detect emission from a unique vibrational state of NO radicals fragmented from NO₂-containing explosive compounds. These compounds, namely TNT, RDX, PETN, are useful although other explosives exist that do not contain the NO₂ functional group. The ability for this technique to detect vapors at ambient conditions in low ppb concentrations is very advantageous. Similar source and optics to other standoff spectroscopic techniques allow for potential integration to occur. Many standoff applications for military use would benefit from such a technique.

6.5.6 Resonance Raman Spectroscopy. UV Raman Spectroscopy follows the same mechanisms described in the Raman Spectroscopy section, although the shorter wavelengths create a resonant enhancement that produces a higher the number of photons available for sensing. In addition, the energy of UV wavelengths allow for more absorption leading to lower limits of detection [3]. There has recently been significant investment in this area with potential for standoff and remote sensing applications. Absorption may diminish the range of materials that could be detected due to competing molecular mechanisms. Recent work demonstrated detection limits in the milligrams per square centimeter within 10 meters from the surface. [88]

Conclusion: The resonance enhancement observed from UV excitation sources provides a more sensitive Raman sensor. Although UV radiation can attenuate and absorb more species in the atmosphere than IR, the enhancement provides lower detection limits than near-IR sources. In addition, explosive analytes may exhibit wavelength dependence regarding absorbance. Stronger absorbance would require even lower amounts of residue

on an interrogated surface. UV Raman shows strong promise for standoff detection of explosives, although limited compact UV sources may restrict accelerated maturation.

6.5.7 Terahertz – Time Domain Spectroscopy (THz – TDS). Terahertz has recently received increased attention and funding for potential bulk detection as well as trace detection solution. THz radiation provides penetration through non-metallic materials while offering unique spectra within the 0.1 – 3.5 THz bandwidth. THz-TDS relies on weak bonding characteristics of molecules for unique signatures. In addition, reflection mode suffers from diffuse reflectance although transmission mode is difficult to envision in the field. For standoff applications, THz radiation is strongly absorbed by water vapor and attenuated by airborne particulates in the atmosphere although recent novel advances may provide a means to generate THz radiation far from the laser source and closer to the target of interest, hence decreasing the atmospheric absorptive effects.

THz-TDS exhibits strong potential as a means of detecting explosive materials due to unique spectral responses. One key advantage is the potential marriage of spectral identification with imaging providing even stronger arguments for using this technology as a means to detect concealed explosives and explosive devices. Practical application of THz-TDS in screening-type and standoff applications is still at early stages of development. Standoff detection of the explosive RDX has been demonstrated to 30 m in a laboratory setting. [88] Current research initiatives have demonstrated the principle of explosives imaging and identification; however, much testing and many refinements are still required before THz detection of explosives in the field becomes feasible. [88]

Conclusion: THz-TDS needs further investigation before proper evaluation of its utility in the field. The advantages of combining unique spectral responses with imaging capabilities offer great standoff detection solutions. Unfortunately, atmosphere effects and high cost, large size equipment would be needed to be effective in the standoff mode. Efforts to create new sources, such as quantum cascade lasers (QCLs), may help its eventual utility.

7.0 Conclusion

This project investigated novel sensor technologies for potential future development with the ultimate goal of improving survivability and situation awareness for the warfighter. Many previous explosive specific sensor technology developments have focused on DHS and TSA applications. Due to the effectiveness of explosive related threats against the U.S. forces, DoD funded development programs have the mission to develop similar sensor solutions. Currently, no “silver bullet” sensor exists that meet the needs of the warfighter to detect explosive threats within military environments. These outdoor, complex, harsh conditions prevent easy transition of COTS sensors. The AFP-based Fido has demonstrated utility for some applications. Typically, current detection systems that provide the best sensitivity, selectivity, response time, detection distance, etc. do not meet SWAP constraints for FCS systems. Therefore, basic and applied research is needed to mature COTS sensors and/or develop novel sensing technology. Due to constraints of SWAP, focus was given to sensor platforms that could be integrated into military systems with the least impact.

Investigation of novel sensor platforms, sensory materials, and standoff sensing was completed in this challenge project. Bulk detection methods were mostly omitted due to difficulty of deployment and SWAP constraints. A brief description of the sensing mechanism or concept was completed for each technology. In addition, information corresponding to the evaluation criterion was included in this paper when supplied in the references. Current cost of sensor systems was not included due to technology immaturity and constantly improving manufacturing processes driven by parallel industries. The list of technologies provided was not intended to be a comprehensive list due to time constraints.

Evidence from many recent published reports support the following conclusions. For sensor platforms, SAW devices and enhancements to IMS offer potential near term solutions due to robustness and are COTS systems that can be modified for military applications. For mid and far-term solutions, microcantilevers and CNTs may hold the best overall potential due to their extremely efficient transduction mechanisms ensuring low detection limits. For sensory materials, combining those described into a sensor array could provide an effective sensing solution. While researching potential AN and UN sensing solution, most of the sensory materials were colorimetric (solution-based), which do not match well with military applications. Fluorescing polymers and biomimetic coatings are believed to potentially offer the most selective and versatile material that could be tailored to many target analytes. Investigation of standoff sensing methods produced a wide variety of technologies that have recently received much attention due to current IED problems in OIF and OEF. LIBS and Resonance Raman sensing methods demonstrated good overall attributes for military applications due to the ability to detect the full range of ERCs and can expand their libraries for new target analytes.

While completing this project, there were a few challenges foreseen for practical application of trace sensing techniques. Assumptions have been made that overlook the

acquisition of target analyte. There were two front end sampling and preconcentration methods discussed in this report that begin to address these issues. Due to low vapor pressure of most explosives, strictly relying on vapor analysis may not be enough for effective sensing. Therefore, a capability to sample and process particulates along with vapors needs to be developed in parallel with sensors. Preconcentration steps will extend response time although it may allow sensors with lower detection limits and high selectivity to be more effective. Given the complex urban environments, front end systems may need to sort through interferences, dust and moisture to separate target analytes.

This reality has led to recent investment surge in standoff sensing methods that require no sample preparation, but lack the overall sensitivity and selectivity that sensory materials provide. The key drawbacks for standoff sensing techniques consist of extremely small interrogation area, the heterogeneity of surfaces, and line-of-sight requirement. In order to respond to these challenges, recent development efforts have focused on imaging techniques that span a large visual space and queue specific areas for secondary interrogation or confirmation by standoff sensing. Ultimately, no silver bullet will be developed that meets the sensing needs of the entire threat space. Therefore, sensor development should focus on specific applications.

8.0 Roadmap of Sensor Maturity

The categories below list sensor technologies that reflect potential near-, mid-, and far-term maturity for deployment in military applications. Naturally, not all these technologies will be developed, but the earlier one can recognize the potential utility, the sooner that sensor solutions can be realized. Since these evaluations are based on the published information, not all papers discuss maturity-related criterion nor do they address all evaluation criterion described earlier in this paper. Without further funding and focused testing, some technologies may never be realized in systems. Since these technologies are all still in the development phase and experiments are completed under different conditions, direct quantitative analysis is limited. Given these constraints, the sensor technologies described in this paper (sensor platform, sensory materials, and standoff sensing) are compiled below.

Sensor platforms

<i>Near</i>	<i>Mid</i>	<i>Far</i>
IMS	Integrated IM-MS	CNTs
ITMS	Microcantilevers	Lab-on-a-chip devices
SAW devices	OTFTs	Microfluidic sampling
Micro-preconcentrator	HT-IMS	Micro-ring Resonators
Subsurface IMS	FP sensor	Nanofibrous membranes
	SERS/SERRS	Self-powered sensors
		PSi microcavities

Sensory Materials

<i>Near</i>	<i>Mid</i>	<i>Far</i>
Pentipycenes	Turn-on Fluorescence	Biomimetic coatings
Photoluminescent part.	Pyrene quenching assay	Pyrrole receptors
		Fluorescent nanofibril
		Cyclodextrin MIPs

Standoff Sensing

<i>Near</i>	<i>Mid</i>	<i>Far</i>
LIBS	PDS	CARS
PF-LIF	DRS	THz-TDS
	Resonance Raman	

8.1 Capability Matrix

Excellent	Very Good	Good	Fair	Poor	N/A	Unknown

Sensor Platforms

	Selectivity	LOD	Response Time	Substances	Recovery	SWAP
IMS						
ITMS						
SAW						
Subsurface IMS						
OTFT						
Integrated IM-MS						
SERS/SERRS						
FP sensor						
Microcantilevers						
HT-IMS						
Lab on chip						
CNTs						
Ring Resonators						
PSi microcavities						
Nanofibrous membranes						

Sensory Materials

	Selectivity	LOD	Response Time	Substances	Reversibility	Detection Distance
Penttiptycenes						
Photoluminescent part.						
Turn-on Fluorescence						
Pyrene quenching assay						
Cyclodextrin MIPs						
Biomimetic Coatings						
Pyrrole receptors						
Fluorescent nanofibril						

Standoff Sensing

	Selectivity	LOD	Response Time	Substances	Reversibility	Detection Distance
LIBS	Yellow	Yellow	Blue	Green	Grey	Green
PF-LIF	Green	Green	Blue	Yellow	Grey	Orange
PDS	Orange	Orange	Blue	Green	Grey	Yellow
DRS	Yellow	Yellow	Blue	Orange	Grey	Orange
Resonance Raman	Green	Orange	Blue	Orange	Grey	Orange
CARS	Green	Red	Blue	Green	Grey	Yellow
THz-TDS	Orange	Yellow	Blue	Green	Grey	Red

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