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<td>This report describes efforts undertaken on a seedling project administered through the Army Research Office. The purpose of the seedling was to identify additive techniques or technologies for THz sensing applications, THz+X. The primary application space of interest was standoff sensing of explosives, followed by chemical and biological agents. Two techniques were identified which might prove useful as additive technologies for THz-based sensing. Each is intended to overcome the pressure broadening which is observed at atmospheric ambient pressure and to allow the collection of high resolution THz spectra in terrestrial applications.</td>
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THz+X Seedling Report

1. Executive Overview

1.1. Scope

In September 2004, Nomadics entered into a seedling project administered through the Army Research Office. The purpose of the seedling was to team Nomadics with Frank DeLucia at Ohio State University and Doug Petkie at Wright State University in order to identify additive techniques or technologies for THz sensing applications, THz+X. Our primary application space of interest was standoff sensing of explosives, followed by chemical and biological agents. Nomadics brought experience with explosives and chemical/biological agents; Drs. DeLucia and Petkie brought experience with THz sensing, sources, and detectors.

1.2. Background

THz technology encompasses the generation and detection of electromagnetic radiation spanning frequencies between 100 GHz and 10 THz. This radiation band has historically been difficult to operate in because of the lack of available emitters and detectors. It lies predominantly above the frequencies attainable from electronic devices, but below the frequencies attainable by optical devices. Though the low frequency end of this band has been employed for years to obtain very high resolution spectra of high altitude atmospheric and interstellar gas mixtures using microwave vacuum tubes, the THz region remains a sort of “last frontier” for spectroscopy and sensing.

The ability of THz radiation to penetrate many opaque insulating materials (clothing, paper, etc.) and to provide such high resolution rotational spectra that the components of an unknown interstellar gas mixture can be identified and quantified has led to a desire to apply THz sensing to terrestrial applications. Significant progress in obtaining improved coverage from both ends of the THz region has been obtained through recent development efforts, and it is desirable to direct future efforts to applications showing the most promise.

1.3. General Results

Most of the scenarios considered in this seedling were determined to have a low probability of success due to the basic physics of the THz-matter interactions required—even if small high power tunable sources and sensitive detectors were available.

Standoff line-of-sight identification of vapor phase materials was deemed problematic due to the effects of pressure broadening on the rotational signature of gases at ambient pressures. In the case of explosives of interest, the additional problem of extremely low vapor pressures and short available pathlengths for vapor near solids increases the difficulty anticipated. For aerosols, the presence of neighboring molecules in the liquid phase hinders molecular rotations that provide THz interaction and further broadens the spectra. Except in very special situations, there is no crystallinity in liquids and the broadening of the THz absorbance is expected to hinder attempts to obtain analyte specificity. Solid phase materials have no rotational spectra, so that—unless there is
crystallinity—the results for solids and liquids should be similar to those obtained with near infrared spectroscopy, which probes molecular vibrational overtones: if the matrix is well known and sampling conditions are well controlled, one can identify components from a limited set of possibilities and perhaps even obtain quantitative readings when high analyte concentrations are available. Under field conditions, such control and foreknowledge of the sample matrix composition is not generally possible. In the case of suspicious clouds, however, the ability to determine that the clouds contain materials other than smoke, dust, or water droplets would be of use, and should (even if the material is not identified) be feasible if sufficient return signal can be obtained.

Because of the ability of THz radiation to penetrate most clothing and to reflect harmlessly from metals and skin, high spatial resolution imaging in the THz is very promising. This is conceptually an evolutionary improvement over millimeter wave imaging and should find wide application once imaging THz emitters and receivers become cost effective and objections from observed populations are overcome. It should also be possible to improve differentiation between materials—in analogy to color vision providing better differentiation than black and white—once broadband or widely tunable THz emitters and frequency specific detector arrays are available. Though its application scope would be limited to detecting concealed weapons, contraband, or explosives, it is likely a viable method for detecting such items concealed under clothing. Lack of specificity due to the nature of the sample limits this approach to a “color” imaging technology that can see through clothing and, though promising, it is already being pursued by many groups.

Another promising technology is the use of Rydberg atoms to convert THz photons into electrons that are then imaged by a photocathode array. This provides an alternative to other THz imaging focal plane arrays, but does not enable a novel technique for detecting explosives, chemical agents, or biological agents and is not discussed further in this report.

1.4. Identified Additive Technologies (Xs)

Two techniques were identified which might prove useful as additive technologies for THz-based sensing. Each is intended to overcome the pressure broadening which is observed at atmospheric ambient pressure and to allow the collection of high resolution THz spectra in terrestrial applications.

The first technique generates an artificial low-pressure environment, as is done for mass spectroscopy. This approach would produce a system with many of the strengths and limitations of an MS-MS system for detecting trace explosives or chemical agents. It would perform in a sniffer configuration and would probably be deployed (at least initially) as a portal or checkpoint instrument. Dramatic improvements in analysis speed, sensitivity, and specificity of response might be obtainable.

The second technique enables THz-matter interaction on a time-scale that prevents interaction with nearby molecules. This approach enables a true standoff system that might be capable of identifying the components of an approaching cloud, and so would be applicable to aerosol or vapor phase detection of chemical or biological agents.
2. Scope
This seedling effort was limited to THz-based detection of explosives, chemical agents, and biological agents. Its primary thrust was to identify additive technologies to enable standoff detection, but point detection was also considered. For each class of analyte a number of applications was identified, anticipated difficulties with a pure THz approach were enumerated, and additive techniques were considered that might address the foreseen difficulties.

For explosives the following applications were considered:
- Improvised Explosive Devices (IEDs) and landmines
- Checkpoint and portals
- Suicide bombers
- Vehicle bombs
- Caches and bomb making facilities
- Package analysis

For chemical agents the following applications were considered:
- Agents in a cloud
- Bodies of water
- Factories and smokestacks
- Package analysis

For biological agents the following applications were considered:
- Agents in a cloud
- Bodies of water
- Factories and smokestacks
- Package analysis
- Breath analysis

2.1. Explosive Materials
The scenarios considered for explosives materials may be described as the detection of bulk explosives enclosed within containers, trace solids contaminating surfaces, airborne particles, and vapors emanating from bulk explosive compositions or surface contamination. These materials (and components of the explosive compositions) are thus available for THz interrogation as bulk solids, as particulates in air or on surfaces, or as vapors.

Explosive materials that were considered are listed in the following two subsections by rough order of perceived importance. Compositions (mixtures) are listed under the highest ranked principal component.

2.1.1. High Priority Materials List

*TNT*
- Amatol (Ammonium Nitrate + TNT)
- Ammonal (Ammonium Nitrate + TNT + Aluminum Powder*
or Ammonium Nitrate + Stearic Acid + Aluminum Powder))
C3 (TNT + DNT + RDX + NC + Tetryl)
Composition B (RDX + TNT)
HBX (RDX + TNT)
H6 (RDX + TNT)
Octol (HMX + TNT)
Pentolite (TNT + PETN)
Pictratol (TNT + Picric Acid)
Tetrytol (Tetryl + TNT)
Torpex (TNT + RDX + Aluminum Powder)
Titonal (TNT + Aluminum Powder)

**RDX**
C4 (RDX, polyisobutylene binder, di(2-ethylhexyl)sebacate plasticizer)
Cyclonite, Hexogen, T4 (aka RDX)
PE4 (RDX)
Demolux (RDX + EGDN)
Semtex H (RDX + PETN)
Semtlex A (PETN + RDX)

**HMX**
Octogen (HMX)

**PETN**

**EGDN**

**Nitroglycerine**
Dynamite (Nitroglycerine)
Cordite (NC+NG)
Gelanite (NC + NG)

**Smokeless Powder**

**Black Powder**

**Ammonium Nitrate**
ANFO (Ammonium Nitrate + Fuel Oil)
Water Gel (Ammonium Nitrate + Magnesium)

**TATP**

**HMTD**

### 2.1.2. Additional Materials List

- TNB
- DNT
- Tri Nitro Napthalene
- Lead Styphnate
- Tetryl
2.2. Chemical Poisons, Irritants, and Vesicants

The scenarios considered for these materials were detection of airborne agents dispersed as vapors or aerosols, detection of contamination by dispersed agents on surfaces, and the detection of bulk agents enclosed within containers. These materials are thus available for detection as vapors, aerosols, bulk liquids, or liquid contamination on or in surfaces.

Chemical agents that were considered are listed in the following subsections by rough order of perceived importance. Precursor materials have not been included in this investigation.

2.2.1. Nerve Agents

G Class
Sarin: O-Isopropyl methylphosphonofluoridate, GB
Soman: O-Pinacolyl methylphosphonofluoridate, GD
Tabun: O-Ethyl N,N-dimethylphosphoramidocyanidate, GA
Cyclosarin, GF

V Class
VX: O-Ethyl S-2-diisopropylaminoethyl methylphosphonothiolate

2.2.2. Blister Agents

Sulfur Mustards, HD
2-Chloroethylchloromethylsulfide
Mustard gas: Bis(2-chloroethyl)sulfide
Bis(2-chloroethylthio)methane
Sesquimustard: 1,2-Bis(2-chloroethylthio)ethane
1,3-Bis(2-chloroethylthio)-n-propane
1,4-Bis(2-chloroethylthio)-n-butane
1,5-Bis(2-chloroethylthio)-n-pentane
Bis(2-chloroethylthiomethyl)ether
O-Mustard: Bis(2-chloroethylthioethyl)ether

**Nitrogen mustards**
HN1: Bis(2-chloroethyl)ethylamine
HN2: Bis(2-chloroethyl)methylamine
HN3: Tris(2-chloroethyl)amine

**Lewisites**
Lewisite 1: 2-Chlorovinylidichloroarsine
Lewisite 2: Bis(2-chlorovinyl)chloroarsine
Lewisite 3: Tris(2-chlorovinyl)arsine

### 2.2.3. Blood Agents
Cyanogen chloride, CK
Hydrogen cyanide, AC

### 2.2.4. Chocking Agents
Phosgene: Carbonyl dichloride
Diphosgene

### 2.2.5. Other
Amiton: O,O-Diethyl S-(2-(diethylamino)ethyl)phosphorothiolate, and corresponding alkylated or protonated salts
PFIB: 1,1,3,3,3-Pentafluoro-2-(trifluoromethyl)-1-propene
3-Quinuclidinyl benzilate (BZ)
Chloropicrin: Trichloronitromethane
Saxitoxin

### 2.3. Biological Disease Agents
The scenarios considered for these materials were detection of airborne agents dispersed as aerosols or powders, surface contamination by dispersed agents, food or water contaminated by agents, and bulk agents enclosed within containers. These materials are thus available for detection as aerosols, airborne powders, bulk liquids, bulk powders, or as liquid or solid contamination on or in surfaces, foods, or water.

#### 2.3.1. High Priority List
Bacillus anthracis (anthrax)
Clostridium botulinum
Yersinia pestis
Variola major (smallpox) and other pox viruses
Francisella tularensis (tularemia)
Viral hemorrhagic fevers
Arenaviruses
LCM, Junin virus, Machupo virus, Guanarito virus
Lassa Fever
Bunyaviruses
Hantaviruses
Rift Valley Fever
Flaviruses
Dengue
Filoaviruses
Ebola
Marburg

2.3.2. Additional List
Burkholderia pseudomallei
Coxiella burnetii (Q fever)
Brucella species (brucellosis)
Burkholderia mallei (glanders)
Ricin toxin (from Ricinus communis)
Epsilon toxin of Clostridium perfringens
Staphylococcus enterotoxin B
Typhus fever (Rickettsia prowazekii)
Food and Waterborne Pathogens
Bacteria
Diarrheagenic E.coli
Pathogenic Vibrios
Shigella species
Salmonella
Listeria monocytogenes
Campylobacter jejuni
Yersinia enterocolitica)
Viruses (Caliciviruses, Hepatitis A)
Protozoa
Cryptosporidium parvum
Cyclospora cayatanensis
Giardia lamblia
Entamoeba histolytica
Toxoplasma
Microsporidia
Additional viral encephalitides
West Nile Virus
LaCrosse
California encephalitis
VEE
EEE
3. Background

3.1. THz Physics

The fundamental characteristics of the THz spectral region are determined by (1) the degrees of freedom of matter to which radiation couples and (2) the relative energies of the terahertz photon $h\nu$, interaction energies between fields and molecular moments, and the thermal quanta $kT$. Table 3.1.1 compares a number of energy scales in units of wave numbers ($1\ \text{cm}^{-1} = 30\ \text{GHz}$). Taking the expansive definition of the THz region to be from 0.1 to 10 THz, the THz spectral region extends from 3.33 cm$^{-1}$ to 333 cm$^{-1}$. Because at 300 K the THz regime extends from $< kT$ to $> kT$, a wide range of phenomena and technologies are encountered. Indeed, at either end the technology is typically less challenging, but many of the attractive features of the THz are less prevalent. For example, high power microwave tubes have been produced at 0.1 THz for many years and the high end (10 THz) is only a factor of three away from the frequency of the CO$_2$ laser.

Table 3.1.1 Energies of atoms and molecules

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<tr>
<td>$kT (300\ \text{K}) = 200\ \text{cm}^{-1}$</td>
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<tr>
<td>$kT (1.5\ \text{K}) = 1\ \text{cm}^{-1}$</td>
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<tr>
<td>$kT (0.001\ \text{K}) = 0.0007\ \text{cm}^{-1}$</td>
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<td>$qE (\text{electron}) &gt;&gt; 100000\ \text{cm}^{-1}$</td>
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<td>$\mu E (1\ \text{D}) ~ 1\ \text{cm}^{-1}$</td>
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<tr>
<td>$\mu B (\text{electronic}) ~ 1\ \text{cm}^{-1}$</td>
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<tr>
<td>$\mu B (\text{nuclear}) ~ 0.001\ \text{cm}^{-1}$</td>
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<tr>
<td>E (rotational) $\sim 1-10\ \text{cm}^{-1}$</td>
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<tr>
<td>E (fine structure) $\sim 0.01\ \text{cm}^{-1}$</td>
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<tr>
<td>IR 300 - 3000 cm$^{-1}$</td>
</tr>
<tr>
<td>FIR 30 - 300 cm$^{-1}$</td>
</tr>
<tr>
<td>MW 1 - 30 cm$^{-1}$</td>
</tr>
<tr>
<td>RF $&lt; 1\ \text{cm}^{-1}$</td>
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3.1.1. Relation between Degrees of Freedom and Spectral Regions

The THz spectral region is ordinarily associated with the rotational degree of freedom of molecules. The electronic scale of both atoms and molecules is much too large to interact with THz radiation, and is typically probed using ultraviolet or visible radiation. Vibrational motions associated with the movement of only a few atoms are also on the wrong energy scale for THz interaction and are better suited for infrared (33 to 3.3 $\mu$m) interrogation. However, it is well known that large collective motions, low lying bending modes, and torsional modes have energies in the THz. Although not extensively studied,
these are important because they offer the potential for THz sensing of large molecules (e.g. biomolecules and explosives) that are of high current interest.

### 3.1.2. Gases vs. Liquids and Solids

The spectral characteristics of gases are profoundly altered when they are condensed into liquids or solids. There are no rotations in a liquid or solid no matter how small the droplet. To be very specific in an important case, because the rotation of the water molecule is inhibited, fog droplets do not attenuate THz radiation, although the classical electromagnetic properties of the droplet can lead to scattering according to the relative size of the wavelength of the radiation and droplet.

### 3.1.3. Linewidths

The linewidths of THz phenomena have significant impact on their usefulness as signatures. In gases near room temperature, the linewidth is set by the collision rate and the pressure—at atmospheric pressure to ~10 GHz. As the pressure is reduced, the collision rate and broadening decrease linearly until the Doppler limit is reached: At 1 THz, this is at a pressure of ~0.1 Torr and a linewidth of 1 MHz. This is a 10000 fold reduction from the linewidth at atmospheric pressure. These narrow lines are the basis of a number of very successful remote sensing and laboratory experiments that have been developed in the THz over the last ~50 years. There is not as simple a picture of the origin of linewidths in solids or liquids, and we simply note that these linewidths are much larger.

### 3.1.4. Sensitivity

For a system in thermal equilibrium, the peak absorption coefficient between levels \( m \) and \( n \) is given by

\[
\alpha_{\text{max}} = \frac{8\pi^2 NF_m v_0^2}{3ckT(\Delta \nu)} |\langle m|\mu|n\rangle|^2
\]  

(1)

where \( N \) is the number of molecules per unit volume, \( F_m \) is the fraction of these molecules in the ground state, \( v_0 \) is the transition frequency, \( \Delta \nu \) is the linewidth, and \( |\langle m|\mu|n\rangle| \) is the dipole matrix element. This interaction strength is a strong function of whether a substance is a gas or a solid and of the molecular properties themselves. Although there are many important details, three are of rather general importance. First, in gases \( F_m \) is a strong function of molecular size. More specifically, large molecules have many thermally populated rotational states and, as a result, a spectrum that consists of many, but relatively weaker lines. Secondly, the impact of the linewidth factor is a very general result from quantum mechanics and applies to both solids and gases. Thus, low pressure gases that are observed in the Doppler limit gain \( 10^4 \) – \( 10^5 \) from this factor. Finally, rotational dipole moments are typically one to two orders of magnitude greater than vibrational dipole moments. As a result, very small amounts of the vapors of small molecules need to be collected for detection, in favorable cases as little as \( 10^{-18} \) moles (less than a femtogram).
3.2. Properties of Explosives

Most explosives are relatively large molecules with relatively low vapor pressures, see Figure 3.2.1 taken from a recent TSA presentation. As molecules become larger, their vapor pressures decrease, and little explosive is available for gas phase detection. Additionally, Figure 3.2.1 is for pure materials; most military explosives are used in compositions, which results in a solid phase solution and can further reduce the saturation vapor pressure. In the case of RDX vs. C-4 (RDX and TNT), there is a 100-fold reduction in RDX vapor pressure [1]. In sampling scenarios, the concentration in sampled air will also be much lower than at saturation. And for standoff sensing scenarios, only a very short pathlength through any vapor plume would be available.

![Molecular weight and estimated vapor pressures for selected explosives. Diagram from a recent TSA presentation.](image)

Figure 3.2.1. Molecular weight and estimated vapor pressures for selected explosives. Diagram from a recent TSA presentation.

For either buried landmines or improvised explosive devices, some vapor may leak, particularly through plastic cases or seals on metal cases. However, this rapidly disperses or condenses on nearby soil or surfaces and thus for standoff sensing scenarios, only a very short pathlength through the vapor plume would be available. Solid particles of explosives may be present as contamination on the outside of cases or even where fingerprints were left [2, 3].

The vapor pressures of the explosives in Figure 3.2.1 are temperature dependent as well, Figure 3.2.2. [4], and can range over a million-fold between 280 K and 400K. However, many explosives degrade at elevated temperatures and only breakdown products may exist from samples at elevated temperatures [4].
3.2.1. Characteristics of TNT

TNT has one of the highest vapor pressures and lowest molecular weights of the military explosives in Figure 3.2.1, and so provides a good test candidate for THz detection. The mass of a TNT molecule is 227.1312 amu (377.1605*10^{-24} g), and its density is approximately 2 g/mL. In dry air it has a saturated vapor pressure of 7.3 ppb (70 pg/mL or 70 ng/L), but is typically several (three) orders of magnitude less concentrated in the air nearby a TNT source. This seems to be because the vapor is very likely to condense on soil/dust particles and has been found to adhere to teflon, glass, quartz, nickel, stainless steel, gold, platinum, copper, fused silica, aluminum, and plastic. Table 3.2.1 correlates the number of molecules, total mass, and vapor concentration for TNT in a liter of dry air at standard temperature and pressure (STP). An expectation of explosives vapor extending about 2 cm from a contaminated surface is reasonable.

Table 3.2.1 Molecules, Mass, and Concentrations for TNT in 1L of dry air at various levels of saturation.

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Mass</th>
<th>&quot;parts per&quot; by mole per Liter at STP</th>
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<tbody>
<tr>
<td>1.000</td>
<td>377.2 yg</td>
<td>/L = 39.26 ppst</td>
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<td>3.000</td>
<td>1.131 zg</td>
<td>/L = 117.8 ppst</td>
</tr>
<tr>
<td>25.00</td>
<td>9.429 zg</td>
<td>/L = 1.000 ppsx</td>
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<tr>
<td>186.0</td>
<td>70.15 zg</td>
<td>/L = 7.303 ppsx [pico-saturated]</td>
</tr>
<tr>
<td>1.000*10^3</td>
<td>377.2 zg</td>
<td>/L = 39.26 ppsx</td>
</tr>
<tr>
<td>2.651*10^3</td>
<td>1.000 ag</td>
<td>/L = 104.1 ppsx</td>
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</tbody>
</table>
Assuming milli-saturation, these results indicate that a THz probe beam passing 2 cm above an exposed solid block of TNT on a dry windless day would be expected to have available approximately 7 ppt of TNT vapor with a pathlength equal to the extent of the TNT block.

The amount of TNT contaminating a surface that might be available for surface sampling or ejection into the air above the surface can also be estimated. A study of TNT particle sizes obtained after detonating a 155-mm howitzer round found that, for high-order detonations, particles smaller than 1 mm contributed most of the mass and surface area (with a power law size distribution). For low-order detonations, 85% of the mass of scattered TNT was in >1cm pieces (or almost 40% of the TNT in the round). Many of these chunks were friable and broke into smaller pieces [5].

Surface contamination of 74 ng/cm² has been measured on plastic encased landmines [3], but depending on the mine type and sampling conditions, ranges from 1 to 500 ng/cm² were common. Table 3.2.2 provides the amount of surface area that must be sampled at 100% collection efficiency in order to collect a particle of TNT for various contamination levels and assumed particle sizes.

<table>
<thead>
<tr>
<th>TNT particle size (µm)</th>
<th>Surface Concentration (ng/cm²)</th>
<th>Area per particle (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
<td>2.000</td>
</tr>
<tr>
<td>10</td>
<td>74</td>
<td>0.027</td>
</tr>
<tr>
<td>10</td>
<td>500</td>
<td>0.004</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>250.000</td>
</tr>
<tr>
<td>50</td>
<td>74</td>
<td>3.378</td>
</tr>
<tr>
<td>50</td>
<td>500</td>
<td>0.500</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>2000.000</td>
</tr>
<tr>
<td>100</td>
<td>74</td>
<td>27.027</td>
</tr>
<tr>
<td>100</td>
<td>500</td>
<td>4.000</td>
</tr>
</tbody>
</table>

### 3.2.2. Characteristics of Other Explosives

RDX has a saturated vapor pressure of less than 0.01 ppb. Co-products of RDX often include TNT. In quantitative THz studies of the solid, the typical attenuation coefficient
was about 40 cm\(^{-1}\) [6]. When trying to crush crystals of RDX, it tended to smear, so that the residue from fingerprints was found to be concentrated in particles larger than 10 microns [7]. In tests done by two different groups [8, 9], RDX weights in a first thumbprint after handling Semtex (collected by acetone washing) are about 4.5 and 3 mg, with the tenth print still containing around 100 ng and the fiftieth print averaging 14 ng (with lower and upper bounds of 3 and 76 ng). In the first few prints, the size distribution had two modes in the 30–150 and 150–350 micron ranges. We can note that a 150-micron-diameter solid particle has 1.8 x 10\(^{-6}\) cm\(^3\) volume and thus contains about 2 microgram of RDX. [10]

TNT, DNT, and RDX in soil will have over 90% of the mass adsorbed to soil solid phase, up to 10% in soil aqueous phase, and less than 10\(^{-6}\) in soil vapor phase [3]. Degradation in soil is much faster in wet soil than dry soil. Estimates of degradation time for TNT have varied from 1 day to 1 year; while RDX is significantly longer (36 years, [11]).

PETN (Semtex A) is even more likely to smear than RDX. Wide, thin plates are more likely than smaller spherical particles. DNT has a saturated vapor pressure of about 500 ppb. 2,4-dinitrotoluene is frequently found as a co-product with TNT, often as a large fraction of the vapor. TATP (triacetone triperoxide) is said to have an extraordinarily high vapor pressure. It can be produced from readily available acetone and hydrogen peroxide. These are also formed as decay products, which subsequently dissipate or break down further, so are only present transiently.

Volatile molecular species such as ethylene glycol dinitrate (EGDN, 1.2x10\(^5\) ppb at 300 K), dimethyldinitrobutane, and mononitroluene have been considered for tagging commercial explosives as a means of source identification, but this is not universally done.

### 3.3. THz/Explosives Interactions

Below is a recent survey of the state of THz-based sensing of explosives. All survey results were for explosives in the solid phase.

#### 3.3.1. Osaka Group

The most thorough study was by Yamamoto, et al. [12] on the THz spectroscopy of C-4 (91% RDX). The spectrum was recorded from 150 GHz – 2.7 THz using a THz-TDS system. Several samples sizes were used (0.4mm—2.3mm) and the analysis included corrections for the etalon effect. Figure 3.3.1 and Table 3.3.1 below summarize their results. The lowest resonance is near ~800 GHz with each line width being ~10cm\(^{-1}\).

#### Table 3.3.1 C-4 (RDX) resonance measurements

<table>
<thead>
<tr>
<th>(\tilde{\omega}_j) [cm(^{-1})]</th>
<th>(\alpha) (at peak) [cm(^{-1})]</th>
<th>(S_j) [10(^{-2})]</th>
<th>(\Gamma_j/2\pi) [cm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.9 ± 0.0</td>
<td>42.7</td>
<td>26.3 ± 0.1</td>
<td>7.3 ± 0.1</td>
</tr>
<tr>
<td>35.5 ± 0.0</td>
<td>21.3</td>
<td>1.4 ± 0.1</td>
<td>3.6 ± 0.3</td>
</tr>
<tr>
<td>45.2 ± 0.1</td>
<td>31.2</td>
<td>3.4 ± 0.3</td>
<td>6.3 ± 0.4</td>
</tr>
<tr>
<td>51.0 ± 0.2</td>
<td>30.7</td>
<td>3.2 ± 0.3</td>
<td>8.6 ± 0.7</td>
</tr>
<tr>
<td>65.7 ± 0.1</td>
<td>~50</td>
<td>5.0 ± 0.3</td>
<td>10.8 ± 0.5</td>
</tr>
<tr>
<td>74.8 ± 0.3</td>
<td>~43</td>
<td>1.9 ± 0.3</td>
<td>10.9 ± 1.1</td>
</tr>
</tbody>
</table>
Figure 3.3.1. THz spectra of C-4 (RDX).

Figure 3.3.2. C-4 spectra in an envelope.
They also performed spectral absorption studies of C-4 contained in a sealed paper envelope with the results shown in the Figure 3.3.2. Since sample thicknesses greater than a few millimeters would result in near complete absorption, they also calculated the reflection spectra of C-4 in packing materials under a range of refractive indices. Calculations showed that the distinctive dispersion curve near 26.9 cm\(^{-1}\) would still be evident and useful for identifying C-4. They did not report any experimental reflection spectra.

### 3.3.2. Los Alamos Group

Funk et al. [13] looked at PBX 9501 (95% HMX) and PBX 9502 (95% TATB) also with a THz-TDS system. In this case, optically thick samples were used (2-6 mm) and corrections for the etalon effect were not needed. The peak of the power spectrum occurred near 300 GHz, so a spectrum was only recorded to ~0.8 THz and is shown in Figure 3.3.3. While it shows no resonances, it should be noted that the first resonance for RDX was ~800 GHz in Figure 3.3.1. The absorption coefficients from both of these studies for the various explosives (RDX, HMX, and TATB) show similar trends in increasing absorption up to 800 GHz.

![Figure 3.3.3. THz spectra of HMX and TATB](image)
3.3.3. PSI Group

Cook et al. [14] also used THz-TDS to study the transmission spectrum of several explosives, Figure 3.3.4. Each sample pellet was a 250 µm thick with thicker samples being opaque at frequencies higher than 2 THz. Additional pellets of HMX and PENT were prepared in a mixture of polyethylene to increase the sample length and allow for truncation of the time domain signal to eliminate the effect of etalons in the spectra. The spectra were qualitatively similar for both samples.

Results for RDX are similar to those of Osaka with a broad peak observed at 810 GHz, corresponding to the strong 26.9 cm\(^{-1}\) peak in Figure 3.3.1. The lack of resonances in the HMX spectra agree with the Los Alamos spectra in Figure 3.3.3, while a peak was observed at 1.84 THz.

In PETN, a peak was observed at 2.01 THz and a weak feature in TNT was observed at 1.7 THz.

All of the peaks were attributed to phonon modes due to the polycrystalline forms of the explosives.

3.3.4. Teraview Group

The THz-TDS spectra from Teraview found online has the spectrum for RDX that is in general agreement with the spectra from Osaka in that three of the strongest resonances seem to match, Figure 3.3.5. Note that PSI also observed the strongest resonance near 800 GHz. Teraview’s spectrum of HMX shows no resonances below 1THz and a
resonance near 1.8 THz, in agreement with both the Los Alamos and PSI spectra, with additional resonances observed above 2 THz. The spectrum of PETN shows a feature near 2 THz, in agreement with PSI. The spectrum of TNT also appears to agree with that of PSI in a peak located near 1.7 THz.

![THz spectra from Teraview of Semtex, PE4, RDX, PETN, HMX, and TNT.](image)

**3.3.5. Cross-group Comparisons**

Solid phase transmission spectra acquired by the Osaka, Los Alamos, PSI, and Teraview groups provide a fairly consistent picture of the observable resonances for HMX, PETN, and TNT (Figure 3.3.6) and for RDX (Figure 3.3.7). However, the sample configuration required to obtain these spectra is not consistent with the configurations that might be expected for explosive identification applications. Additionally, the absorbance features observed, though repeatable, are broad and unlikely to be useful in identifying mixtures of explosives or even pure solid explosives in a field environment.

**3.3.6. Additional Groups – Wisconsin**

The Wisconsin group, using all-electronic harmonic multiplication techniques [15, 16], reported several resonances in the reflection spectra of various plastic explosive samples in the range from 50-400 GHz. When considering the signal to noise of the spectra, the evident problem with the etalon effect, and comparisons with other spectra, these results seem very suspect. Figure 3.3.8 is a comparison of the spectra of HMX between the Wisconsin and Los Alamos Groups. The top plot is of the Los Alamos spectra and the bottom is the Wisconsin spectra. Given the agreement and more careful studies by the Osaka and Los Alamos groups, it seems more than likely that the Wisconsin spectrum should not be considered reliable at this time.
Figure 3.3.6. HMX, PETN, and TNT spectra from PSI (top three) and Teraview (bottom).

Figure 3.3.7. RDX spectra from PSI (top), Osaka (middle), and Teraview (bottom).
4. General Results
For all scenarios considered, the broad absorbance features of the THz-matter interaction at ambient pressures are expected to provide very limited ability to specifically identify target analytes. Because of this, many of the application scenarios discussed below are addressed by sampling into a low pressure environment prior to THz interrogation. Additionally, a degradation stage is expected to be required for most targets in order to produce small molecules which are visible to THz spectroscopy.

4.1. Explosives Detection
The scenarios considered for explosives materials may be described as the detection of bulk explosives enclosed within containers, trace solids contaminating surfaces, airborne particles, and vapors emanating from bulk explosive compositions or surface contamination. These materials (and components of the explosive compositions) are thus available for THz interrogation as bulk solids, as particulates in air or on surfaces, or as vapors.
4.1.1. Bulk Solids
In applications related to detection of bulk solid explosives, a THz-based system would operate in an imaging mode rather than a spectroscopic mode. The broad absorbance peaks available from THz spectra of solids or liquids would not be expected to enable identification of materials in a complex background.

<table>
<thead>
<tr>
<th>Application</th>
<th>Feasibility</th>
<th>Discussion</th>
</tr>
</thead>
<tbody>
<tr>
<td>IEDs</td>
<td>No</td>
<td>IEDs are almost always encased in metal to provide shrapnel from detonation. THz cannot see through the metal to the interior explosives</td>
</tr>
<tr>
<td>Checkpoints and Portals</td>
<td>High</td>
<td>Operating as an imaging technique, THz provides inspection through clothing. Metal nails/balls packed around charge to increase damage will also provide enhanced THz visibility. Multi-band THz should provide “color vision” equivalent and increased ability to discriminate explosives from surrounding materials.</td>
</tr>
<tr>
<td>Suicide Bombers</td>
<td>High</td>
<td>Ability to image hidden materials under clothing of individuals.</td>
</tr>
<tr>
<td>Vehicle Bombs</td>
<td>No</td>
<td>No ability to see into vehicles due to metal body.</td>
</tr>
<tr>
<td>Caches and Bomb making facilities</td>
<td>Low</td>
<td>Low possibility of through-wall imaging, and no special ability to detect bulk explosives because lot of things in a building might visually resemble bomb making equipment</td>
</tr>
<tr>
<td>Package Analysis</td>
<td>Low</td>
<td>X-Ray vision systems should provide much greater resolution and imaging capability when X-Ray exposure can be tolerated. THz imaging easily defeated by metal foil.</td>
</tr>
</tbody>
</table>

4.1.2. Particles in Air or on Surfaces
In particle sensing applications, the broad absorbance peaks available at atmospheric pressure would not enable specific identification of explosives. Decomposing the particles and resultant molecules in a low pressure environment should provide a complex THz spectrum of sharp absorbance lines which could be analyzed to determine the existence and identity of explosive molecules present in the original particle with high probability. This is especially true if an aocusto-optic detection approach can be developed to provide sensitivity with a small THz interaction volume.

<table>
<thead>
<tr>
<th>Application</th>
<th>Feasibility</th>
<th>Discussion</th>
</tr>
</thead>
<tbody>
<tr>
<td>IEDs</td>
<td>Low</td>
<td>Requires close proximity to IED to collect samples from surface or in air nearby. Path to sufficiently small, low power systems for this application is unclear.</td>
</tr>
<tr>
<td>Checkpoints and Portals</td>
<td>High</td>
<td>When combined with low pressure and decomposition, THz holds potential to provide suitable sensitivity with dramatic specificity improvement over existing particle analysis</td>
</tr>
</tbody>
</table>
techniques.

<table>
<thead>
<tr>
<th>Application</th>
<th>Feasibility</th>
<th>Discussion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suicide Bombers</td>
<td>Low</td>
<td>Requires close proximity to suicide bomber to collect samples. Path to sufficiently small, low power systems for this application is unclear.</td>
</tr>
<tr>
<td>Vehicle Bombs</td>
<td>Low</td>
<td>Requires close proximity to vehicle to collect samples. Path to sufficiently small, low power systems for this application is unclear.</td>
</tr>
<tr>
<td>Caches and Bomb making facilities</td>
<td>Moderate</td>
<td>When combined with low pressure and decomposition, THz holds potential to provide suitable sensitivity with dramatic specificity improvement over existing particle analysis techniques. Portability is a concern.</td>
</tr>
<tr>
<td>Package Analysis</td>
<td>High</td>
<td>When combined with low pressure and decomposition, THz holds potential to provide suitable sensitivity with dramatic specificity improvement over existing particle analysis techniques.</td>
</tr>
</tbody>
</table>

4.1.3. Vapors

Same as for Particles in air or on surfaces but with increased sampling time due to preconcentration requirements.

4.2. Chemical Agent Detection

The scenarios considered for these materials were detection of airborne agents dispersed as vapors or aerosols, detection of contamination by dispersed agents on surfaces, and the detection of bulk agents enclosed within containers. These materials are thus available for detection as vapors, aerosols, bulk liquids, or liquid contamination on or in surfaces.

4.2.1. Vapors

For vapor sensing applications, broad THz peaks would be expected due to atmospheric broadening. Specific identification of chemical agents would generally require intimate contact with the agent in order to interrogate it in a low pressure environment.
<table>
<thead>
<tr>
<th>smokestacks</th>
<th>expected to be unavailable sampling into a low pressure system.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Package analysis</td>
<td>Moderate</td>
</tr>
</tbody>
</table>

### 4.2.2. Aerosols

Aerosols are not expected to provide any meaningful THz signal due to a lack of molecular rotational freedom in liquids. THz radiation may be able to penetrate aerosol clouds to interrogate vapor between the aerosol particles, however. When intimate contact with the sample is permitted, a low pressure THz detection approach similar to that described for explosive particles should provide sensitivity and selectivity.

### 4.2.3. Bulk Liquids

The results for bulk liquids should be similar to those for aerosols, except that sample collection would need to be adapted. Additionally, a metal container would shield bulk liquids from interrogation.

### 4.2.4. Liquid Contamination on or in Surfaces.

The results for liquid contamination should be similar to those for aerosols, except that sample collection would need to be adapted.

### 4.3. Biological Agent Detection

The scenarios considered for these materials were detection of airborne agents dispersed as aerosols or powders in a cloud, surface contamination by dispersed agents, food or water contaminated by agents, and bulk agents enclosed within packages. These materials are thus available for detection as aerosols, airborne powders, bulk liquids, bulk powders, or as liquid or solid contamination on or in surfaces, foods, or water.

In biological sensing applications, the THz energy is believed to couple to low energy vibrational modes supported by the extremely large biological molecules. These molecules often possess a limited degree of crystallinity. Additionally, there is the possibility of THz interaction with related materials used to support biological growth, to provide enhanced biological stability, or to enable more effective distribution.

#### 4.3.1. Airborne Powders

In the case of airborne powders the situation is more promising. In the solid phase, the crystallinity arising from a regular arrangement of bio-molecules (as exists in anthrax spores, for example) would allow a THz interaction. The problem then arises that the THz absorbance features would be broad and provide only limited specificity. Intimate sampling and breaking the biological molecules into smaller molecules that could be probed in a low pressure environment would not provide specificity in this case because harmless and virulent biological samples are constructed from the same basic materials. Growth or stabilization media may also provide broad signatures that could be used to identify anomalous clouds, if they provide a crystalline structure upon drying.
4.3.2. Aerosols

For aerosol sensing applications, no meaningful THz signal would be expected due to a lack of molecular mobility within the aerosol droplet. Additionally, the large biomolecules would not provide a meaningful vapor that could be probed, as may be the case for a chemical agent. Thus THz interrogation is not expected to provide useful information when probing biological agent aerosols unless there are high vapor pressure THz-visible small molecules that are known to accompany biological agents.

4.3.3. Bulk Liquids

Same as for aerosols

4.3.4. Bulk Powders

<table>
<thead>
<tr>
<th>Application</th>
<th>Feasibility</th>
<th>Discussion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface contamination</td>
<td>Low</td>
<td>Interaction pathlength with biomolecules is short and the broad THz peaks would be difficult to interpret against the varied THz signal background due to the THz-surface interaction.</td>
</tr>
<tr>
<td>Food or water contamination</td>
<td>Low</td>
<td>Signal from biomolecules lost in signal from food matrix. Moisture content of most foods would also render them opaque.</td>
</tr>
<tr>
<td>Package analysis</td>
<td>Low</td>
<td>Some ability to determine that a package contains biological material. However package constructions permitting such interrogation are very limited.</td>
</tr>
</tbody>
</table>
5. Identified Additive Technologies (Xs)

5.1. **Low Pressure Approach**

In the case where intimate sampling is permitted—at checkpoints, within airhandling systems, and for package analysis—an opportunity for a low pressure THz+X approach exists. One of the primary strengths of THz spectroscopy is the sharpness and strength of the absorbance features available when interrogating low pressure gasses. The problem of application to explosives, chemical agents, and biological agents is that these materials are natively large molecules that are deployed at atmospheric pressure. The key is to convert the large target molecules into smaller molecules that are THz-visible and to bring them into a vacuum, where their spectra narrow and strengthen.

Beyond the availability of a functional low pressure THz spectrometer, three conditions must be met in order for this approach to be feasible:

1) Sufficient target material must be collectable into the system
2) The target material must be degradable into THz-visible small molecules
3) The distribution of THz-visible small molecules must be specific to the target material

Condition 1 limits the deployment conditions to those in which the target material can be intimately sampled and, unfortunately, eliminates standoff applications from this approach. Once the technology is developed and miniaturization proceeds, it may be possible to produce system that could be set into suspect clouds and similar situations, but this would not be feasible immediately. The need to collect sufficient target material also pushes toward particulate or aerosol sampling for low vapor pressure molecules, such as many chemical agents and most explosives.

Condition 2 provides the forward connection from target molecule to THz visibility but may also limit deployment scenarios. Natural degradation pathways for explosives, for example, are not fully predictable or controllable. The sample collection system must provide pyrolytic or enzymatic breakdown (as examples) of the target molecule. Different processes would require different support in the instrumentation. Pyrolytic decomposition could be performed using heaters, but those draw power; enzymatic decomposition would require reagents, which may have limited shelf life.

Condition 3 allows the backward connection between the THz-visible molecules and the target molecules. This condition is the one which eliminates biological molecules from this approach. Since biomolecules are generally constructed from the same basic building blocks, even full characterization of the small molecule population and concentrations arising from breakdown of large biomolecules would not be expected to allow determination of the originating target biomolecule, though one could likely definitively state that it was a biomolecule. Chemical agents tend to have unusual molecular structure and would be expected to produce molecules that could be back-linked to the originating agent. The case is also strong for sensing explosives, but less strong (though still quite possible) for being able to identify specific explosives in mixtures. A list of papers addressing the breakdown products of explosives is provided in the Appendix.
5.2. Interaction Prevention Approach

In this section we will discuss a scheme which combines a THz probe with a pump CO$_2$ laser in a double resonance scheme, Figure 5.2.1, that has much in common with laboratory energy transfer studies as well as with swept gain super-radiance optically pumped FIR lasers.

![Figure 5.2.1 THz+X Pump Probe Approach.](image)

Figure 5.2.1 THz+X Pump Probe Approach.

Figure 5.2.2 shows the energy levels of the basic scheme in the context of a molecule with well known energy transfer properties, CH$_3$F. In this approach a pulsed laser is used to transfer population, on the time scale of the atmospheric collisional relaxation ($10^{-10}$ sec), from a rotational level in the ground vibrational state, to a rotational level in the excited vibrational state. On the upper right of the figure is shown the modulation on the THz absorption signature produced by the pump laser on the rotational signature in each of the vibrational states. On the lower right is shown the net modulation. This modulation will have the time scale of the pulse sequence of the pump laser, modified by molecular relaxation mechanisms.

![Figure 5.2.2 Effect of infrared pump upon THz-active molecular absorbances.](image)

Figure 5.2.2 Effect of infrared pump upon THz-active molecular absorbances.

The advantages of this approach over the usual THz remote sensing schemes are several fold:
1. Because at atmospheric pressure lines in the atmosphere are relatively broad (~10 GHz), without this modulation the resonances are difficult to separate from system variations, atmospheric variability, and background clutter. Since the pump modulates the system with a well-defined pulse sequence, these problems are eliminated - this is a very important gain.

2. The broad lines also significantly impact the specificity of species identification. In this double resonance scheme the 1-D specificity matrix (the THz resonance frequency) is augmented by the 1-D matrix associated with the pump frequency, and another 1-D matrix associated with the time delay between the pump and probe. This results in a 3-D matrix and significantly enhances specificity, Figure 5.2.3.

![3D Specificity Matrix](image)

Figure 5.2.3 3D Specificity Matrix.

Additionally, in this limit there is an increase in the absorption/emission coefficient equal to the reciprocal of the fractional population difference between the upper and lower rotational levels in thermal equilibrium. Because at 250 GHz the fractional population difference between the upper and lower rotational levels is only 1/20, the empty level created by the pump increases the interaction strength of the rotational transition by a factor of 20 by elimination the stimulated emission/absorption cancellation, Figure 5.2.4.
Thus, if the equilibrium absorption coefficient for CH$_3$F is $10^{-2}$ cm$^{-1}$, over a 1 km path with a 1 ppm concentration the pump modulated a 250 GHz beam over this path by 2%. This is a very large modulation by the standards of the sensitivity of THz systems.

This effect is shown in the context of a large molecule whose individual spectral lines are unresolved at atmospheric pressure in the figure. One can see that not only is a modulated signature imposed on the equilibrium absorptions, but also that the modulated signatures are 20 times larger than the equilibrium absorption.
6. Conclusions

Most of the scenarios considered in this seedling were determined to have a low probability of success due to the basic physics of the THz-matter interactions required—even if small high power tunable sources and sensitive detectors were available.

Standoff line-of-sight identification of vapor phase materials was deemed problematic due to the effects of pressure broadening on the rotational signature of gases at ambient pressures. In the case of explosives of interest, the additional problem of extremely low vapor pressures and short available pathlengths for vapor near solids increases the difficulty anticipated. For aerosols, the presence of neighboring molecules in the liquid phase hinders molecular rotations that provide THz interaction and further broadens the spectra. Except in very special situations, there is no crystallinity in liquids and the broadening of the THz absorbance is expected to hinder attempts to obtain analyte specificity. Solid phase materials have no rotational spectra, so that—unless there is crystallinity—the results for solids and liquids should be similar to those obtained with near infrared spectroscopy, which probes molecular vibrational overtones: if the matrix is well known and sampling conditions are well controlled, one can identify components from a limited set of possibilities and perhaps even obtain quantitative readings when high analyte concentrations are available. Under field conditions, such control and foreknowledge of the sample matrix composition is not generally possible. In the case of suspicious clouds, however, the ability to determine that the clouds contain materials other than smoke, dust, or water droplets would be of use, and should (even if the material is not identified) be feasible if sufficient return signal can be obtained.

Two techniques were identified which might prove useful as additive technologies for THz-based sensing. Each is intended to overcome the pressure broadening which is observed at atmospheric ambient pressure and to allow the collection of high resolution THz spectra in terrestrial applications.

The first technique generates an artificial low-pressure environment, as is done for mass spectroscopy. This approach would produce a system with many of the strengths and limitations of an MS-MS system for detecting trace explosives or chemical agents. It would perform in a sniffer configuration and would probably be deployed (at least initially) as a portal or checkpoint instrument. Dramatic improvements in analysis speed, sensitivity, and specificity of response might be obtainable.

The second technique enables THz-matter interaction on a time-scale that prevents interaction with nearby molecules. This approach enables a true standoff system that might be capable of identifying the components of an approaching cloud, and so would be applicable to aerosol or vapor phase detection of chemical or biological agents.
7. References


8. Appendix: Explosives Degradation Products

Initial Reaction(s) in Biotransformation of CL-20 Is Catalyzed by Salicylate 1-Monooxygenase from Pseudomonas sp. Strain ATCC 29352; Applied and Environmental Microbiology, July 2004, p. 4040-4047, Vol. 70, No. 7; [http://aem.asm.org/cgi/content/full/70/7/4040 (FULL ARTICLE)]


Characterization of Metabolites during Biodegradation of Hexahydro-1,3,5-Trinitro-1,3,5-Triazine (RDX) with Municipal Anaerobic Sludge; Applied and Environmental Microbiology, June 2000, p. 2652-2657, Vol. 66, No. 6; [http://aem.asm.org/cgi/content/full/66/6/2652 (FULL ARTICLE)]

Biodegradation of Hexahydro-1,3,5-Trinitro-1,3,5-Triazine and Its Mononitroso Derivative Hexahydro-1-Nitroso-3,5-Dinitro-1,3,5-Triazine by Klebsiella pneumoniae Strain SCZ-1 Isolated from an Anaerobic Sludge; Applied and Environmental Microbiology, November 2002, p. 5336-5341, Vol. 68, No. 11; [http://aem.asm.org/cgi/content/full/68/11/5336 (FULL ARTICLE)]


Dissolution rates of three high explosive compounds: TNT, RDX, and HMX; Chemosphere, 2002 May;47(7):725-34; [http://www.ncbi.nlm.nih.gov/entrez/query.fcgi?db=PubMed&cmd=Retrieve&list_uids=12079068&dopt=Citation (ABSTRACT)]


Biotransformation of Hexahydro-1,3,5-Trinitro-1,3,5-Triazine (RDX) by a Rabbit Liver Cytochrome P450: Insight into the Mechanism of RDX Biodegradation by Rhodococcus

Biodegradation of the Hexahydro-1,3,5-Trinitro-1,3,5-Triazine Ring Cleavage Product 4-Nitro-2,4-Diazabutanal by Phanerochaete chrysosporium; Applied and Environmental Microbiology, February 2004, p. 1123-1128, Vol. 70, No. 2; [http://aem.asm.org/cgi/content/full/70/2/1123?view=full&pmid=14766596 (FULL ARTICLE)]


Analysis of RDX and RDX breakdown products in environmental samples; [http://emsp.em.doe.gov/workshop_pdfs/new_orleans_2003/poster_session/Felt.pdf (FULL ARTICLE)]


Biological Degradation of 2,4,6-Trinitrotoluene; Microbiology and Molecular Biology Reviews, September 2001, p. 335-352, Vol. 65, No. 3; [http://mmbr.highwire.org/cgi/content/full/65/3/335 (FULL ARTICLE)]
9. List of Publications Supported

Papers published in peer-reviewed journals
None

Papers published in non-peer-reviewed journals or in conference proceedings

Papers presented at meetings, but not published in conference proceedings
None

Manuscripts submitted, but not published
None

Technical reports submitted to ARO
None

List of all participating scientific personnel showing any advanced degrees earned by them while employed on the project
None

Report of Inventions
None

Bibliography
None

Appendices
None