Improved Detection of Explosive Residues by Laser Thermal Desorption

John S. Morgan, Wayne A. Bryden, Joseph A. Miragliotta, and Leonard C. Aamodt

Detection of explosives has become a high priority for counterterrorism and land mine clearance operations. In most cases, current technology relies on detection of the metal casing of a mine or explosive device. Because dogs can directly detect explosive residues in air, it is theorized that an “artificial nose” could be constructed to provide fast, reliable detection of explosives. One major obstacle to this approach is the low vapor pressure of explosive materials, such as RDX, at ambient temperature. It is possible, however, to momentarily increase the explosive vapor pressure in the headspace over a target by the use of laser thermal desorption. In this sampling technique, a laser pulse of appropriate wavelength is focused onto a target spot and a detector momentarily samples the vapor over the target. Thus, highly sensitive vapor detectors could be used to detect explosive residues on surfaces of interest. (Keywords: Desorption, Detection, Explosive, Land mine, Laser.)

INTRODUCTION

Typically, the cost to construct and place an anti-personnel land mine runs from $3 to $15 per unit. The cost of land mine clearance, however, can exceed $1000 per unit. Humanitarian demining operations are not expected soon to clear large areas of Bosnia, Cambodia, Angola, or other regions with dense concentrations of land mines. In addition, the presence of anti-personnel and larger land mines hampers the effectiveness of attacking ground troops. Without large land mine breaching systems, ground troops are forced to use decades-old techniques that expose demining engineers to severe risk.1 Finally, unexploded ordnance remains a problem at recently decommissioned bomb and gunnery ranges.

Most current explosive detection technology is based on finding metallic objects through eddy current detection. The Defense Advanced Research Projects Agency (DARPA) is now seeking to augment that technology with devices that detect the vapor from explosives and their degradation products. Bomb-sniffing dogs perform remarkably well at this task, being capable of detecting levels of explosive vapor in the low part-per-billion range.2 Canine olfaction does not function by identifying a particular substance with a specific sensor. Instead, the collective response of many signals enables a dog to recognize a particular odor. Further, dogs localize odors efficiently by repeated inhale/exhale cycles, and may even sample particles of up to 100 μm
by breathing on and thereby disturbing the surface particles.

It may be possible to emulate a dog's nose by using a suite of nonspecific vapor detectors with a collective response that is unique to a particular odor. Several technologies are being investigated for this purpose, including thin-film resonators, adsorbent polymers, and genetically engineered proteins. All of these detectors are compromised by the extremely low vapor pressure of explosive compounds at ambient temperatures, as seen in Table 1.\(^3\)

However, there is one alternative solution. If the target is momentarily heated, the vapor pressure will increase substantially, thus allowing for detection of the explosive. As indicated in Table 1, this strategy significantly enhances detectability. For example, the room temperature vapor pressure for 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) is in the part-per-trillion range of detectability, a range very difficult to detect. However, at 100\(^\circ\)C, the compound can be found at part-per-million levels.

This strategy is assisted by the natural transport of explosive material from a buried land mine to the ground surface. Over time, especially if the ground is somewhat wet for even a short period, explosive material inside a land mine will slowly diffuse through the soil to form a very thin crust of explosive and explosive degradation products on the ground surface. Of particular interest is the presence of 2,4-dinitrotoluene (2,4-DNT), which is now believed to be the primary means by which dogs detect explosives, owing to its relatively high vapor pressure. Normally, this crust lasts for some time since ambient temperatures are unlikely to cause significant sublimation of the surface crust. If a laser or other pulsed source of thermal energy is applied to the surface crust, a momentary increase in the concentration of explosive vapor will occur in the headspace over the ground, thus allowing for detection by the "electronic dog's nose" sensor. These pulses do not possess sufficient energy to detonate the explosive material, particularly when the primary interest is in detection of low-concentration residues.

APL's effort under the DARPA program is focused on this strategy of laser thermalization of trace explosives in ground crusts. The study is divided into three thrusts: modeling of the laser–surface interaction; controlled experiments using a quadrupole mass spectrometer and various laser front ends; and testing of the sampling system with detectors engineered for highly sensitive response to explosive vapor.

### MODELS OF THE LASER–SURFACE INTERACTION

The laser–surface interaction was modeled in two ways. In the first case, temperature profiles were calculated by assuming that radiation is incident on a semi-infinite absorbing slab in sequenced pulses of specific duration. This model, developed by R. L. McCally of APL and S. Favin (APL retiree) for application to laser irradiation of eye corneas, does not account for thermal radiation and convective heat transfer.\(^4\) Further, it is inherently a single-layer case because it cannot take into account the light and thermal pulse transmission at buried interfaces. For example, the effect of a water overlayer cannot be considered. In this model, the laser beam is defined by its beam profile or width, power per unit area, and pulse width. The target is defined by its density, specific heat, thermal conductivity, and absorption coefficient at the laser wavelength. The model outputs a temperature profile as a function of time for a given depth into the sample and distance from the center of the laser profile.

Carbon dioxide (CO\(_2\)) laser heating of two substrates, alumina and silica, was considered in the initial analysis. Alumina has an absorption coefficient of 397/cm at 10.6 \(\mu\)m, the wavelength at which CO\(_2\) lasers operate. This value is similar to that of silica, which has an absorption coefficient of 415/cm at 10.6 \(\mu\)m. The thermal conductivity of alumina, 0.825 cal/cm-sec-\(^\circ\)C, is, however, much higher than that for silica, which is 0.00318 cal/cm-sec-\(^\circ\)C. Silica is quite similar to many "real-world" targets, including fuller's earth, sand, and limestone.

**[Figure 1](#)** shows a typical output of CO\(_2\) laser heating of alumina. The temperature rise during the 100-ns pulse was considered separately from the temperature decay profile, which was considered starting from 10 \(\mu\)s.

### Table 1. Physical properties of the most common explosives.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vapor pressure (25(^\circ)C, torr)</th>
<th>Detection threshold</th>
<th>Vapor pressure (100(^\circ)C, torr)</th>
<th>Detection threshold</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4,6-Trinitrotoluene (TNT)</td>
<td>(5.8 \times 10^{-6})</td>
<td>8 ppb</td>
<td>(0.105)</td>
<td>138 ppm</td>
</tr>
<tr>
<td>1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX)</td>
<td>(4.6 \times 10^{-9})</td>
<td>6 ppt</td>
<td>(9.0 \times 10^{-5})</td>
<td>0.12 ppm</td>
</tr>
<tr>
<td>Nitroglycerin (NG)</td>
<td>(0.0025)</td>
<td>3 ppm</td>
<td>(6.0)</td>
<td>7800 ppm</td>
</tr>
<tr>
<td>Pentaerythritol tetranitrate (PETN)</td>
<td>(5.6 \times 10^{-8})</td>
<td>0.07 ppb</td>
<td>(8.4 \times 10^{-4})</td>
<td>1.1 ppm</td>
</tr>
</tbody>
</table>
The calculation from Fig. 1 assumes a CO\textsubscript{2} laser pulse of 100 mJ, with a 0.5-mm beam radius. The temperature increase is roughly 200\textdegree C at both the surface and a depth of 5 mm. Similarly, at 100 mJ/pulse, the temperature increase is well over 1000 \textdegree C.

In Fig. 2, it is observed that the surface of silica, with its low thermal conductivity, can be heated very easily. A 10-mJ/pulse CO\textsubscript{2} laser produces a temperature increase of nearly 400 \textdegree C. In Fig. 3, the depth profile of this heating is examined. At a depth of 1 or 10 \textmu m, significant heating still exists, not unlike that seen at the surface. At 50 to 100 \textmu m, the heating is much less, though it does increase at later time intervals. This behavior is due to the movement of a thermal pulse from the surface down into the material as time passes. Thus, modeling indicates that it is relatively straightforward to produce temperature increases in ideal substrates sufficient to volatilize common explosive compounds.

A second model was also examined. Based on the laser irradiation of composite materials for thermal wave imaging, this model takes into account multilayer effects, such as a thin layer of water on the top of the target soil. However, the model does not include more complex effects such as the energy losses associated with the heat of vaporization of water. Lateral heat flow is also ignored, so that the model produces one-dimensional solutions to the two-layer case. It is based on representing the pulsed-laser–initiated heat flow as a Fourier transform in frequency space, where the boundary conditions must match at each interface. In the simple case of a one-layer material irradiated with a narrow beam, the temperature \( T \) at a depth \( L \) and time \( t \) in a material with thermal diffusivity \( \alpha \) will vary as

\[
T \propto \exp(-L^2/4\alpha t) / t .
\]

In the multilayer case, thermal reflections must also be considered, complicating the analysis.

Typically, a CO\textsubscript{2} laser will produce 150-ns pulses with an energy density of 2.4 mJ/mm\textsuperscript{2} for an unfocused beam, though much higher energy densities can be achieved with a well-focused beam. If we consider a 2-\textmu m water overlayer and a silicon oxide (SiO\textsubscript{2}) target, this laser energy will produce temperature increases of roughly 80\textdegree C at the interface, as seen in Fig. 4. The temperature of the water layer exceeds 100\textdegree C during the first microsecond after the laser pulse, with subsequent cooling shown by the response at 25 and 75 \mu s. In practice, the target temperature would be limited to below 100\textdegree C due to water vaporization. Laboratory experiments indicate that temperatures as low as 70\textdegree C are
sufficient to allow for the detection of explosive residues. Further, a water overlayer will tend to be much less than 2 mm deep, and its presence will actually increase the explosive residue available for detection owing to enhanced transport from a buried mine to the surface of the ground.

Inside the SiO$_2$ at depths greater than 2 mm, the temperature increase is more modest than that observed at the surface, but the thermal pulse causes higher temperatures within the bulk of the sample at later times, as occurred in the single-layer case. The water layer’s effect appears to be limited to a decrease in the peak temperature at the surface of the SiO$_2$ (roughly a factor of 3) and a lengthening of the time constant associated with the decaying temperature profile.

EXPERIMENTAL VARIATION IN INCIDENT LASER POWER AND WAVELENGTH

A test stand (Fig. 5) was constructed to examine the effect of variations in laser power and wavelength to determine the optimum system for laser thermalization. In addition, it was theorized that the explosive vapor plume from an irradiated target could be sampled at an optimum time to maximize the concentration of explosive-containing vapor for detection. Thus, a very fast-pulsed valve was used to sample the headspace vapor over the target of interest at various times during and after the initial laser pulse. This valve could open for as little as 150 μs.

Both neodymium:yttrium-aluminum-garnet (Nd:YAG) and CO$_2$ lasers were used, as seen in Table 2. These lasers operate in the infrared portion of the electromagnetic spectrum and are therefore well suited to heating targets without decomposing the analytes of interest. The absorption coefficient of most materials, including the targets used here (soils and SiO$_2$), is much lower at 1.06 mm, the Nd:YAG wavelength, than at 10.6 mm, the CO$_2$ wavelength. Thus, it is not unexpected that the CO$_2$ lasers performed much better than their Nd:YAG counterparts, even at comparable power levels. However, Nd:YAG lasers can be more easily miniaturized, thus making them interesting subjects for study. Two Nd:YAG lasers were used: a very small, centimeter-sized, diode-pumped laser from the Massachusetts Institute of Technology Lincoln Laboratory (MIT/LL) and a small commercial benchtop Nd:YAG laser from Continuum, Inc. The Continuum MiniLite 3315 produces 25 mJ/pulse at 10 Hz with a 5- to 7-ns pulse width at high power.

For the Nd:YAG studies, silica/RDX targets were used in which RDX constituted approximately 700 ppm of the target composition. The MIT/LL laser did not produce detectable levels of RDX vapor, nor did the Continuum MiniLite 3315 at low power. At high power, transient pulses of RDX vapor were produced, though high-mass RDX fragments were not seen. For a mass-to-charge ratio (m/z) of 46 (corresponding to the NO$_2$ fragment of RDX), the peak intensity increased from a minimal baseline at the time of the Nd:YAG laser pulse and decayed over a period of a few tenths of a millisecond. This behavior was not observed for higher mass fragments (such as m/z = 120 or 128), perhaps because the effect is small compared to the inherent system noise.

Two different CO$_2$ lasers were used: continuous-wave and pulsed. The continuous-wave laser was
chopped using a Uniblitz mechanical shutter capable of shutter speeds as fast as 5 ms. In this setup, RDX fragments were easily observed when the target was located inside the vacuum system near the mass spectrometer source. A typical RDX spectrum obtained in this way is seen in Fig. 6, where 50% laser power (25 mW) and 50-ms open-shutter cycles were used. The fragments observed in this spectrum were almost entirely from RDX, including characteristic peaks at 120, 128, and 148 amu. The molecular ion at amu 222 was not observed because of dissociation in the electron-impact ionization source of the mass spectrometer. This result is similar to that seen with the bulk heating of RDX-containing samples to between 70 and 100°C. In contrast to the modeling predictions, the decay time of RDX fragments occurred over a period of several hundred milliseconds, most likely due to the bulk heating of the target.

Targets were also excited with a pulsed CO₂ laser from Laser Science, Inc., capable of 10 mJ/pulse at 10-Hz repetition rates. In this case, the target was not bulk heated, and RDX fragments were detected only when the target was inside the vacuum system. Outside the vacuum system, in each case, explosive residue condensed on the walls of the pulsed-valve inlet. In addition, the low duty cycle of the pulsed valve (less than 0.1%) prevented the efficient detection of transient increases in the vapor concentration of explosive material.

**TESTING WITH ALTERNATIVE DETECTORS**

To determine whether the laser sampling could work with alternative detectors, the pulsed CO₂ laser was tested with an ion mobility spectrometer (IMS), a commonly used detector for explosives, drugs, and process monitors. The IMS, a Photo-Chem 110 with a Model SF-12 air sampler provided by the Idaho National Engineering and Environmental Laboratory, measures the average time for a group of ionized vapor molecules to traverse a chamber of dense gas under the influence of an electric field.

The IMS could not detect RDX near its source inlet in the absence of a laser thermalization source. When the pulsed CO₂ laser was focused onto an RDX/soil target, however, the IMS easily detected the RDX vapor produced within a few seconds. A small signal could

<table>
<thead>
<tr>
<th>Laser type</th>
<th>Wavelength (mm)</th>
<th>Pulse width (μs)</th>
<th>Pulse energy (μJ/pulse)</th>
<th>RDX detected (in vacuo)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd:YAG (MIT/LL)</td>
<td>1.06</td>
<td>200</td>
<td>2</td>
<td>No</td>
</tr>
<tr>
<td>Nd:YAG (Continuum MiniLite)</td>
<td>1.06</td>
<td>5</td>
<td>25</td>
<td>*</td>
</tr>
<tr>
<td>CO₂ (CW, chopped)</td>
<td>10.6</td>
<td>50</td>
<td>1.2</td>
<td>Yes</td>
</tr>
<tr>
<td>CO₂ (pulsed, Laser Sciences, Inc.)</td>
<td>10.6</td>
<td>100</td>
<td>10</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Note: CW = continuous wave; Nd:YAG = neodymium:yttrium-aluminum-garnet; LL = Lincoln Laboratory.
*Detection not definitive from data.
be obtained from TNT targets in the absence of laser excitation. With the pulsed CO\textsubscript{2} laser, however, TNT was rapidly detected, even in small concentrations.

These tests conclusively showed that the sensitivity of a continuous-flow detector is enhanced by the increase in the headspace vapor concentration of analyte provided by laser thermalization. Further experiments were conducted using sensors from Rockwell Science Center and the California Institute of Technology. Rockwell has developed a thin-film resonator that is coated with polymers. The resonant frequency of the resonator shifts when explosive vapor is absorbed by the polymer material. The California Institute of Technology sensor consists of resistive films of polymer and carbon. The polymer swells when it absorbs explosive vapor, thus causing the resistance of the mixed films to increase.

In both experiments, the signature of 2,4-DNT was used as a primary standard because recent tests indicate that this degradation product is prevalent in the area around buried land mines. Further, 2,4-DNT has a higher equilibrium vapor pressure than other compounds that are present, making detection easier. Both sensors can detect the saturated headspace vapor over neat 2,4-DNT, such as in a closed bottle containing crystals of this substance. In open air, however, neither sensor detected 2,4-DNT vapor in an airstream flowing from a sample to the sensor area. Under laser excitation, however, the concentration of this vapor was sufficiently increased to permit rapid detection by both sensors. They did not detect 2,4-DNT in soils, however, even under laser excitation.

**SUMMARY**

Detection of explosive residues has become a major priority for mine clearance and counterterrorism. Application of technologies that emulate the broad sensor capabilities of the canine nose may solve the explosive detection problem. These technologies can be enhanced by sampling methods that increase the available headspace vapor concentration of explosive residues in the vicinity of targets of interest.

**REFERENCES**


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IMPROVED DETECTION OF EXPLOSIVE RESIDUES

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