



TECHNICAL REPORT  
NATICK/TR-03/010

AD \_\_\_\_\_

**DETECTION OF LANDMINES AND SUSPECTED  
MINEFIELDS USING NOVEL AMPLIFYING  
FLUORESCENT POLYMERS**

by  
**Marcus la Grone  
Mark Fisher  
Colin Cumming  
and  
Eric Towers**

**Nomadics, Inc.  
Stillwater, OK 74074**

December 2002

Final Report  
April 2000 – June 2001

Approved for public release; distribution is unlimited

Prepared for  
**U.S. Army Soldier and Biological Chemical Command  
Soldier Systems Center  
Natick, Massachusetts 01760-5020**

20030114 053

## DISCLAIMERS

The findings contained in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of trade names in this report does not constitute an official endorsement or approval of the use of such items.

## DESTRUCTION NOTICE

### For Classified Documents:

Follow the procedures in DoD 5200.22-M, Industrial Security Manual, Section II-19 or DoD 5200.1-R, Information Security Program Regulation, Chapter IX.

### For Unclassified/Limited Distribution Documents:

Destroy by any method that prevents disclosure of contents or reconstruction of the document.

**REPORT DOCUMENTATION PAGE**

*Form Approved  
OMB No. 0704-0188*

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

**PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE (DD-MM-YYYY) 11-12-2002		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) April 2000 - June 2001	
4. TITLE AND SUBTITLE DETECTION OF LANDMINES AND SUSPECTED MINEFIELDS USING NOVEL AMPLIFYING FLUORESCENT POLYMERS				5a. CONTRACT NUMBER C-DAAD16-00-C-9242	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Marcus la Grone, Mark Fisher, Colin Cumming, and Eric Towers				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Nomadics, Inc. 1024 S. Innovation Way Stillwater, OK 74074				8. PERFORMING ORGANIZATION REPORT NUMBER 1057024B	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Sponsor: Defense Advanced Research Projects Agency (DARPA) Advanced Technology Office (Thomas Altsuler) 3701 North Fairfax Drive Arlington, VA 22203-1714				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) NATICK/TR-03/010	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited					
13. SUPPLEMENTARY NOTES Monitor: US Army Soldier and Biological Chemical Command, Soldier Systems Center, ATTN: AMSSB-RSS-MA(N) (T. Gilroy), Natick, MA 01760-5020					
14. ABSTRACT This report describes continuing efforts to detect landmines by using novel fluorescent polymers that sense the ultra-trace concentrations of nitroaromatic compounds emanating from explosives contained in mines. Under this contract, scientific studies were made and several new generations of detectors were developed and tested in an effort to understand the chemical signature of landmines. It has been shown that the landmine chemical signature tends to be heterogeneous and can be dispersed in the environment near the mine location. This makes it difficult to pinpoint the exact location of the mine using trace chemical detection methods. However, evidence currently available indicates that it may be possible to isolate a mine location to within a small, well-defined area. Also discussed in this report is a promising method for standoff detection of suspected mines using small beads coated with the amplifying fluorescent polymer. Nomadics was able to demonstrate the detection of the quenching effect at a distance of 58 meters.					
15. SUBJECT TERMS LANDMINES                      DETECTION TECHNOLOGY                      CHEMICAL SIGNATURES MINEFIELDS                      FLUORESCENT POLYMERS                      LOCATION AID DEVICES MINE DETECTION                      NITROAROMATIC COMPOUNDS                      TRACE CHEMICAL DETECTION DETECTORS                      EXPLOSIVES					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Thomas Gilroy
U	U	U	SAR		19b. TELEPHONE NUMBER (Include area code) 508-233-5855

## Contents

List of Figures .....	v
Preface .....	vii
1. Introduction .....	1
2. Overview of System Hardware .....	2
2.1 Fido Sensor Overview .....	2
2.2 Sampling Equipment .....	4
2.3 Gas chromatograph.....	5
3. Field Test Results of the Nomadics Sensor .....	6
3.1 Yuma Proving Ground Tests.....	6
3.2 Sensor Conclusions.....	11
4. Standoff Landmine Detection Using Amplifying Fluorescent Polymers.....	11
4.1 Introduction.....	11
4.2 Standoff Test Bed .....	12
4.3 Standoff Detection Conclusions.....	15
References.....	16

## List of Figures

Figure 1.	Description of Polymer Quenching Amplification Mechanism .....	3
Figure 2.	A Schematic of a Fido Sensor Prototype .....	4
Figure 3.	Electrostatic Particle Sampler (ESPC) .....	4
Figure 4.	Response of Fido to a 50-picogram Reference Standard Mix and a Soil Particle Extract Collected over a TM62P3 Landmine .....	7
Figure 5.	Mine Lane at Yuma Proving Ground .....	7
Figure 6.	Sensor Responses for Samples Collected Perpendicular to Mine Lane .....	9
Figure 7.	Contour Map of Fido TNT Response for Square Grid.....	10
Figure 8.	Preliminary Results Showing Detection of Quenching from a Distance .....	12
Figure 9.	Optical Test Bed Photos .....	12
Figure 10.	Optical Test Bed System Diagram .....	13
Figure 11.	Standoff Detection System Elements .....	14
Figure 12.	Standoff Detection - Results of Introduction of Contaminated Samples .....	15

## **Preface**

This report describes the engineering development, field tests, and scientific conclusions of an ultra-sensitive chemical trace landmine detection system. The effort was funded by the Defense Advanced Projects Agency (DARPA) and the contract, number C-DAAD16-00-C-9242, was administered by the U.S. Army Soldier Systems Center, Natick, MA. The effort was conducted by Nomadics, Inc. of Stillwater, OK, between April 2000 and June 2001.

# DETECTION OF LANDMINES AND SUSPECTED MINEFIELDS USING NOVEL AMPLIFYING FLUORESCENT POLYMERS

## 1. Introduction

Once a landmine is deployed, a complex process begins in which the environment near the mine slowly becomes contaminated with explosives and related compounds (ERCs) derived from the parent explosive [1-5]. The extent of the contamination depends on a number of variables including mine type, the condition of the mine casing, soil type, soil moisture content, burial depth, soil topography, the density and type of vegetation, and the length of time elapsed since mine emplacement. The distribution of signature compounds in the environment can be highly heterogeneous, often with small areas of relatively high contamination dispersed among a larger area of little measurable contamination. A surprising finding is that the mine chemical signature is not necessarily strongest directly over the mine. Further, the mine signature often extends past the perimeter of the mine, sometimes to a significant distance from the mine center. The direction of dispersal of signature has also been observed to be non-symmetrical and can be influenced by factors such as the topography of the soil near the mine [3, 6]. Information gained from studies of soil and vapor samples collected from minefields is crucial to gaining an understanding of how landmine signatures develop over time, and data from field testing of cutting edge chemical sensors and sampling equipment are also adding to this knowledge base.

The emerging picture is that pinpointing the exact location of a mine using trace chemical sensors is difficult for a number of reasons. Not the least of these reasons is that the chemical signature of mines can be widely dispersed in the environment. However, the fact that the dispersed chemical signature can be detected by trace chemical sensors suggests that these devices can be used to signal the presence of a minefield as opposed to pinpointing the exact location of individual mines within the field. This detection paradigm differs from most in use today that rely on various mine detecting technologies to locate the exact position of targets. Approaches that seek to locate exact target positions require that every square meter of an area be screened for individual mines. In contrast, an area reduction technique, such as trace chemical detection, could be used to determine whether or not dispersed explosive signatures are present in an area, indicating that a minefield may be present. Once an area is deemed suspect, technologies that can pinpoint the exact location of the mines can be used to facilitate removal of the mines. If successful, this will enable demining efforts to focus on areas that actually contain mines, rather than consuming significant resources in areas that are not mined.

The detection of landmine trace chemical signatures has focused primarily on detection of explosives in the vapor phase and in soil. While further study is required, there is some evidence that the signature can also be detected in vegetation. While concentrations of target analytes vary significantly from site to site, the concentration of TNT in soil over mines is rarely more than a few parts-per-million (ppm) by mass and is often orders of magnitude less. Detection of target analytes in the vapor phase is even more difficult. The concentration of TNT and ERCs in the air over contaminated minefield soils is often five to six orders of magnitude less than the concentration in the soil [4, 7]. As the distance from the mine increases, these concentrations become even lower. Hence, very sensitive detection technologies are needed to detect the trace chemical signature produced by a mine.

Soil TNT concentrations in the low parts-per-billion (ppb) can be detected by only a few laboratory instruments, such as gas chromatographs (GC) utilizing electron capture detectors (ECD). Because soil concentrations of TNT and related compounds near mines are often lower than the detection limits of standard devices, field investigation of landmine chemical signatures, particularly dilute signatures displaced significantly from the mine center, has been difficult. Nomadics, Inc. initiated development of an extremely sensitive detector for TNT (known as Fido) under the Defense Advanced Research Projects Agency (DARPA) Dog's Nose Program [8–10]. Improvements to the system have made it possible to detect landmine chemical signatures in the field and in lab samples at concentrations two to three orders of magnitude lower than that of commercially available state-of-the-art laboratory sensors. This system detects signature compounds in the vapor phase and from contaminated soil particulates collected from an area of user-determined size (from a few square centimeters to many square meters). Preliminary results from field tests of this system that demonstrate its possible use as a minefield area reduction tool are extremely promising.

## **2. Overview of System Hardware**

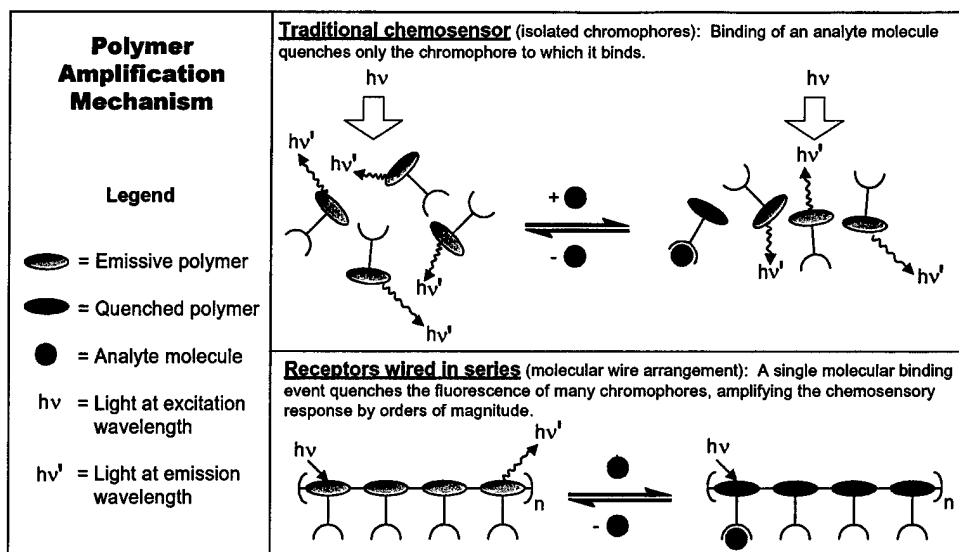
### **2.1 Fido Sensor Overview**

To our knowledge, Fido was the first person-portable field sensor to detect the chemical vapor signature of a landmine under field conditions. In blind field tests administered by DARPA at Ft. Leonard Wood, Missouri, the sensor was able to detect TMA5 and PMA1A landmines with the fuses and detonators removed, with shipping plugs capping the detonator well. These field tests are described in detail elsewhere [8–10]. Canines were also tested at the site during these tests. The performance of Fido was comparable to that of the canines in this test [5].

The sensor system has been described in detail elsewhere, so only a brief description will be presented here. Fido utilizes novel fluorescent polymers developed by collaborators at the Massachusetts Institute of Technology as sensory materials. These polymers were specifically engineered to detect TNT [11–14], the explosive found in excess of 85% of mines now deployed [15]. Conventional fluorescence detection normally measures an increase or decrease in fluorescence intensity that occurs when a single molecule of analyte interacts with a single fluorophore. The upper right frame of Figure 1 illustrates a transduction mechanism of this type.

In these novel polymers, binding of a single TNT molecule quenches the fluorescence of many polymer repeat units, thereby amplifying the effect of a single TNT binding event. When thin films of these polymers absorb a photon of light, excited state electrons (i.e., “excitons”) are able to efficiently migrate along the conjugated polymer backbone [13] and between adjacent polymer chains. During its excited state lifetime, the exciton propagates by a random walk through a finite volume of the polymer film. If an electron-deficient (i.e., electron accepting) molecule such as TNT binds to the polymer film, a low-energy “trap” is formed. If the exciton migrates to the site of the bound electron-deficient molecule before transitioning back to the ground state, the exciton will be trapped (a non-radiative process), and no fluorescence will be observed from the excitation event. Since the exciton samples many potential analyte binding sites during its excited state lifetime, the probability that the exciton will sample an occupied “receptor” site and be quenched is greatly increased. In practice, there is evidence that these polymers result in an amplification of quenching response of between 100- and 1,000-fold as





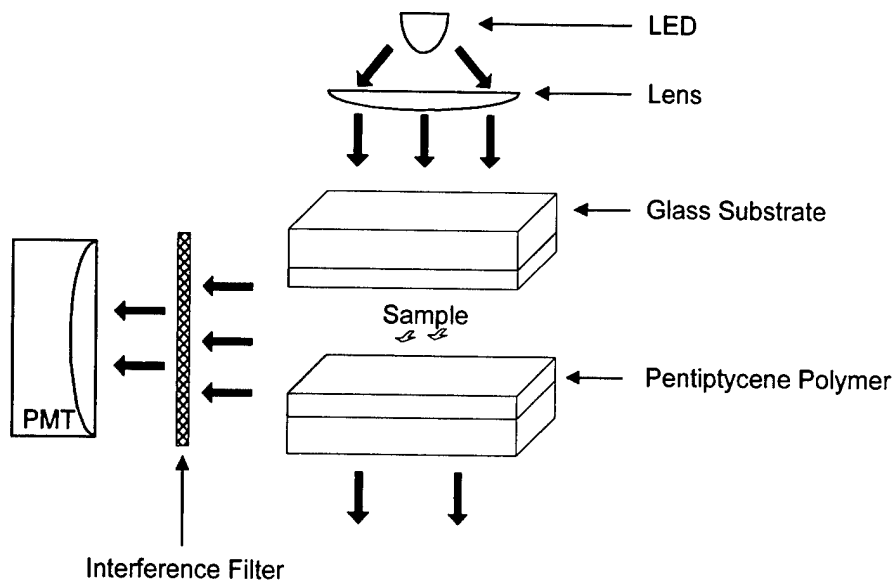
**Figure 1. Description of polymer quenching amplification mechanism.**

compared to conventional (monomeric) quenching mechanisms. The resulting amplification is a key factor in achieving the exceptional sensitivity of the detector, which has been demonstrated in laboratory tests to have a minimum detection limit for TNT of approximately 1 femtogram ( $1 \times 10^{-15}$  grams).

Amplifying fluorescent polymers (AFP) are engineered to be preferentially responsive to nitroaromatic explosives. The polymers, which are electron-rich, are believed to bind reversibly to electron-deficient nitroaromatics through an electrostatic-type interaction. By synthesizing structures into the polymer that are electrostatic mirror-images of target analytes, selectivity is improved via enhanced, preferential electrostatic interactions between the polymer and target analytes relative to potential interferents. In addition, by matching the reduction potential of the analyte to the effective ionization energy of the polymer, additional selectivity is achieved.

A schematic of a Fido sensor is shown in Figure 2. A blue light-emitting diode (LED) or laser diode serves as the excitation source. Light from the source is focused at normal incidence onto two glass substrates coated with thin films of the polymer. The glass substrates act as planar waveguides for light emitted by the polymer and define the sensor sample chamber. The light exiting the edge of the substrate travels through an interference filter that passes light emitted by the polymer but blocks a significant fraction of stray light from the excitation source. A photomultiplier tube (PMT) or photodiode then measures the fluorescence intensity.

Air that may contain target analyte vapors is drawn through the sampling chamber by a small pump. If the air contains vapors of target analytes, the intensity of the fluorescence registered by the PMT will decrease proportionally to the mass of analyte that binds to the polymer films. The operator is then alerted to the possible presence of ERCs. The response of the sensor to target analytes is almost instantaneous upon sample introduction, enabling near real-time analysis of samples. Because binding of analytes to the films is reversible, the same polymer film can be exposed repeatedly to samples. A flow of clean air over the films will desorb analyte from the films, returning the fluorescence intensity to near the initial baseline reading.



**Figure 2. A schematic of a Fido sensor prototype.**

## 2.2 Sampling Equipment

Field samples are collected by one of three methods. The first method is direct, real-time sampling of vapor-phase samples using the Fido sensor. Of the three methods utilized, this method provides the most position-sensitive data, enabling well-resolved location of signature "hot spots." The volumetric sampling rate of the sensor in this mode is low, sampling only vapors located in the immediate vicinity of the sensor inlet. No sample preconcentration is utilized in this mode. The concentration of the vapor-phase signature over mines is often in the low parts-per-trillion (ppt) concentration range or lower. This concentration is five to six orders of magnitude less than the concentration of ERCs in the contaminated soil producing the vapor signature [3, 4]. Hence, the success of this sampling method is influenced more heavily by minefield conditions at the time of sampling. Favorable conditions for vapor phase signature detection include warm temperatures, light winds, and damp soil conditions. This is likely due to the fact that the vapor phase concentration of ERCs over explosive contaminated soils has been shown to increase with soil moisture content [5, 7]. The vapor pressure of TNT also increases sharply with temperature, so warm temperatures also favor increases in vapor concentration. High winds tend to rapidly disperse the vapor signature, especially in the absence of vegetation over the mine. To date, the best performance of a Fido sensor sampling directly from the ambient was a 100% probability of detection with a 10% false alarm rate. This performance was achieved during tests administered by the Defense Advanced Research Projects Agency (DARPA) at Ft. Leonard Wood [8].

The second method of sampling is by use of an electrostatic soil particle collector (ESPC) Fig. 3. The ESPC consists of two electrodes and an air jet to gently



**Figure 3. Electrostatic particle collector (ESPC).**

dislodge soil particles from the ground. The outer electrode is an electrically conductive cylinder through which the air with entrained dust particles is drawn by a small pump. The second electrode is a small diameter rod located on the axis of the cylinder. A corona is generated within the cylinder by applying a high voltage across the electrodes. As soil particles are drawn through the cylinder they become highly charged because of the action of the corona discharge. The electrostatically charged soil particles are attracted to and stick primarily to the outer cylindrical electrode. After a sampling cycle, power to the electrodes is switched off, and the particles are dislodged from the electrodes into a sampling vial. Explosives on the soil are then extracted into acetone, and the extract is presented to Fido for analysis via a portable gas chromatograph. The electrodes are cleaned after use and are then reused. With this device it is possible to collect a sample of finely divided soil particles from over a relatively large area.

The final sampling method involves sampling both soil particles and vapor by drawing samples through a bed of adsorbent material designed to trap vapors of ERCs. Soil particles are also trapped in the bed. Air is drawn at high volumetric flow rates through the cartridge containing the adsorbent medium, enabling rapid sampling of large volumes of air and entrained particulates. The cartridge is mounted at the end of a long handle through which air is drawn by a high-volume pump. The long handle enables the operator to stand upright while holding the sampler inlet near the ground to collect samples. After a sample is collected, the cartridge is removed from the handle, and any trapped analyte is extracted into solvent and presented to Fido via a portable gas chromatograph (see below). Alternatively, trapped vapors can be liberated by thermally desorbing the trap directly into the sensor. Samples can be collected very rapidly with this device from large areas, and the inexpensive sampling cartridges are disposable.

### **2.3 Gas chromatograph**

A Fido sensor interfaced to a modified SRI Model 8610 gas chromatograph (GC) is currently being used to analyze soil particle samples collected with the ESPC and the high-volume sampling cartridges. Analyte is extracted from the cartridges into a solvent, and the extracts are then introduced into the chromatographic system. The gas chromatograph enables separation of the solvent from sample constituents, allowing the solvent to be vented from the sensor. In addition, the chromatographic retention data greatly improves system selectivity. The system uses air as a carrier gas, is portable, can be used in the field, and can perform analysis of a sample in under two minutes. Because of the selectivity of the sensor, complex sample matrices containing hundreds of compounds produce very simple chromatograms with few peaks other than target nitroaromatic compounds. With so few responses, adequate chromatographic resolution can be achieved even with rapid temperature ramp rates and short analysis times.

While not a viable solution for most minefield applications, the GC capability provided by this system is enabling collection of data that have proven extremely useful in development of an integrated sensor/high-volume sampling package. An integrated high-volume sampling and sensor combination is currently being designed utilizing lessons learned from the chromatograph/sensor package.

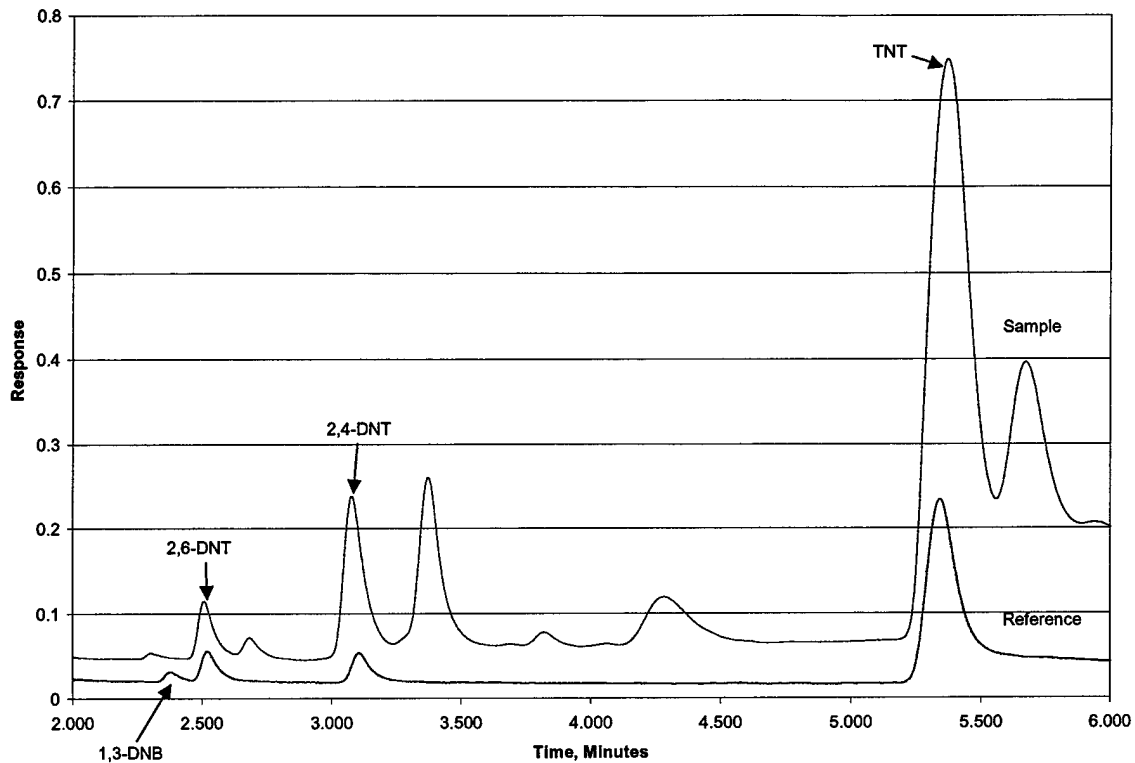
### 3. Field Test Results of the Nomadics Sensor

#### 3.1 Yuma Proving Ground Tests

In January 2001, Nomadics personnel conducted field tests of the previously described equipment at Yuma Proving Ground (YPG), Arizona. Testing of Fido sensors via two modes of sampling (soil particle and vapor-only sampling) was conducted.

The YPG is located in a harsh, high desert environment. The soil is coarse sand with little organic content. At the time of the tests, the soil was extremely dry as there had been no measurable precipitation for the prior six months. It has been shown that the primary mode of explosive transport through soil is through the movement of soil water [4]. Water from rain tends to carry explosives deeper into the soil, while movement of soil water toward the surface of the ground during soil drying phases (evapotranspiration) tends to transport explosive signatures to the soil surface where they are deposited onto surface soils as the water evaporates. Photodecomposition of ERCs on surface soils by the action of sunlight can lead to the degradation of surface ERC signatures over time. Hence, the absence of movement of significant soil moisture for a long period of time reduced the transport of signature compounds to the soil surface where they could be detected. Consistent with these factors, the concentration of ERCs in most surface soils at YPG was very low and below the detection limits of our laboratory GC with an electron capture detector (ECD). An ECD is one of the more sensitive commercially available laboratory detectors for explosives, with a detection limit of approximately 10 picograms for TNT. However, Fido interfaced to the SRI 6890 was able to detect explosive signatures in many soil samples collected with the ESPC. Figure 4 illustrates the response of Fido to a reference standard solution containing 50 picograms of 1,3-dinitrobenzene, 2,6-dinitrotoluene, 2,4-dinitrotoluene, and TNT. These are compounds frequently found in the chemical signature of landmines [1, 3, 5]. Superimposed on this chromatogram is the response of Fido to a soil particle sample extract collected over a TM62P3 landmine. Responses to 2,6-dinitrotoluene, 2,4-dinitrotoluene, and TNT are clearly visible. Other unknown peaks in the chromatogram are visible. Some of these may be due to other nitroaromatics not in the reference standard mix, or potential interferents that are easily distinguished from target analytes due to their chromatographic retention times.

Unfortunately, conditions at the site were not conducive to detection of vapor phase ERCs. As previously discussed, the vapor pressure of explosives over contaminated soils is highly dependent on soil moisture content. As the soil moisture content increases, the headspace vapor concentration of explosives also increases. Because the soil moisture content was so low, vapor phase ERC concentrations throughout the test period were too low to detect. Rain (0.06 inches) did fall at the site during the night after the second day of testing, but the soil quickly dried the next morning. In addition, the surface soil ERC concentration was so low before the rain that any enhancement in vapor concentration due to wet soils after the rain was still below detection limits. Hence, the rainfall had no lasting positive effect on vapor sensing. Soil particle samples taken on the days after the precipitation did show a trend of general increase in ERC concentrations, indicative of transport of ERCs to the surface of the ground as the soil moisture evaporated after the rain. Again, this general increase in soil ERC concentrations was too modest to facilitate vapor phase sensing after the rain. This is in contrast to a series of experiments conducted at a previous field test at Ft. Leonard Wood in which dry minefield soils



**Figure 4. Response of Fido to a 50-picogram reference standard mix and a soil particle extract collected over a TM62P3 landmine.**

produced no detectable vapor signature until watered. After a small amount of water was applied to the soil, vapor signatures were readily detected by Fido and by canines on site.

There were five lanes from which samples were taken at Yuma. Samples were also taken from a square, gridded area. The lanes and the square area were divided into cells marked with string or very light rope. Each of these cells was labeled. The lanes were divided into two columns designated as column "A" or "B". Each column was divided into 50 cells, assigned an integer label in the range of 1 to 50 (Fig. 5). The lanes were divided into a total of 100 cells with dimensions of 0.5 meters long by 0.75 meters wide. On the square, labels were similar, but the range of letters was "A" through "J" and the range of numbers was 1 through 10, producing a square array of 100 cells of 1.5 meters on each side.



**Figure 5. Mine lane at Yuma Proving Ground.**

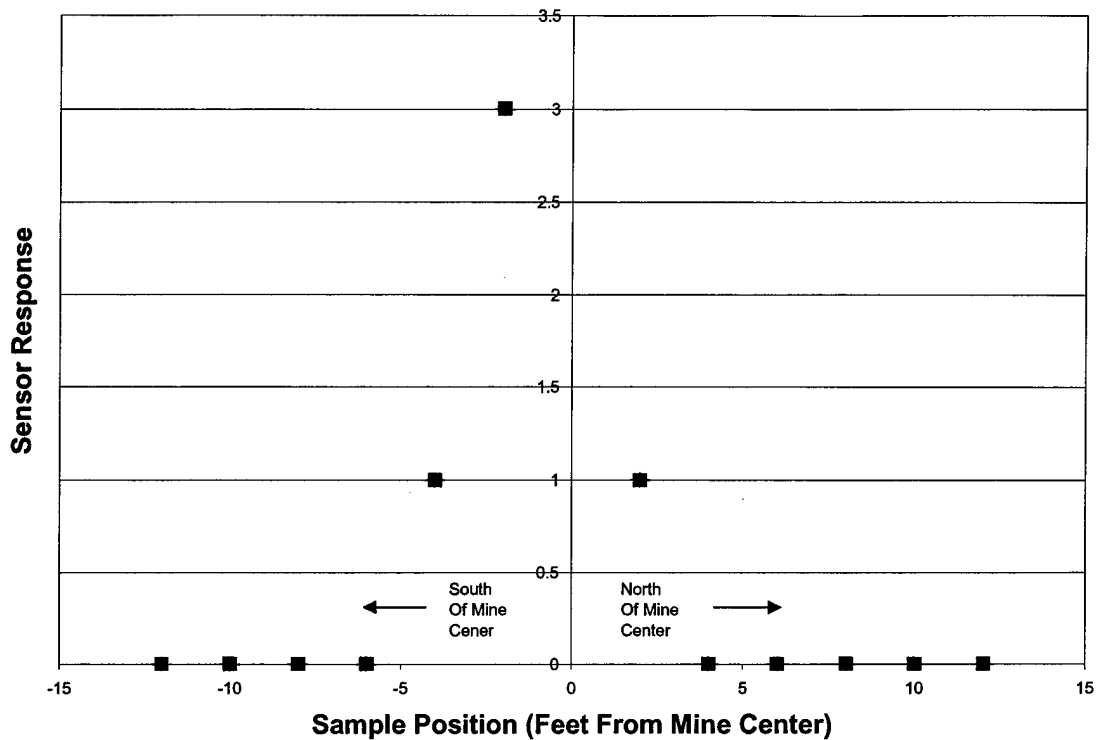
Particle samples were taken from each cell in each lane and from the square grid. An attempt was made to sample the entire area in each cell. After extraction into acetone, analysis of each sample by GC/Fido was performed. The chromatographic results were then submitted for independent analysis. By comparing the behavior of the Fido/SRI GC system when run on very low concentration calibration standards, we came to believe that the Fido/SRI GC system was extremely capable of discriminating interferences from ERCs and detecting very low concentrations of explosives.

Unfortunately, the initial interpretation of test results was disappointing because explosive signatures in the soil within the lanes appeared to be widespread and not well correlated with mine locations. The initial hypothesis was that widespread contamination of the site had occurred because of frequent detonation of explosive devices at the site and due to certain range management practices. To test this hypothesis, a follow-up trip was performed two months after the initial sampling event. The goal of this trip was to collect soil samples from areas near but outside the mine lanes from which the samples had been previously collected in January. The intention was to collect many "blank" samples from the site to confirm or refute the hypothesis that the site was widely contaminated with explosives.

When the soil samples from the second trip were analyzed, it was quite evident that away from the mine lanes chemical signatures consistent with the presence of explosives were seldom detected. This refuted the hypothesis that the site was widely contaminated with ERCs. Of the 74 "blank" samples collected, only 2 were found to contain significant explosive signatures. Traces of TNT at concentrations barely above the detection limit of Fido were found in 5 samples collected near a heavily traveled road on the site. No "blank" samples with detectable ERCs were observed anywhere else on the site. Soil samples were again taken from within some of the same mine lanes sampled in January and were again found to contain explosive signatures. In the second trip, it was found with greater than 95% confidence that explosive signatures were distributed inside the mine lanes, but not outside of the lanes. However, the distribution of explosive signature within lanes was still not well correlated with known mine positions.

Additional data supporting the conclusion that explosive signatures were present within the mine lanes but were absent outside the lanes was obtained during the second trip. Multiple samples were collected along a line that ran perpendicular to the length of a mine lane. This line was selected so that it crossed over the top of a mine in the lane. Twelve samples were taken at +/- 2, 4, 6, 8, 10, and 12 feet north and south from the mine (Fig. 6). Only four hits were recorded. TNT and DNT were found in samples at 2 feet South. TNT was recorded in samples taken at 4 feet south and 2 feet north. Hence, samples collected at points along the line on both sides of the lane (but outside of the lane) were blank, but explosive signatures were detected in the samples taken from inside the mine lane. The data indicate that the detection radius of Fido around this mine was ~1.75 m +/- 1.0 m (with 95% confidence).

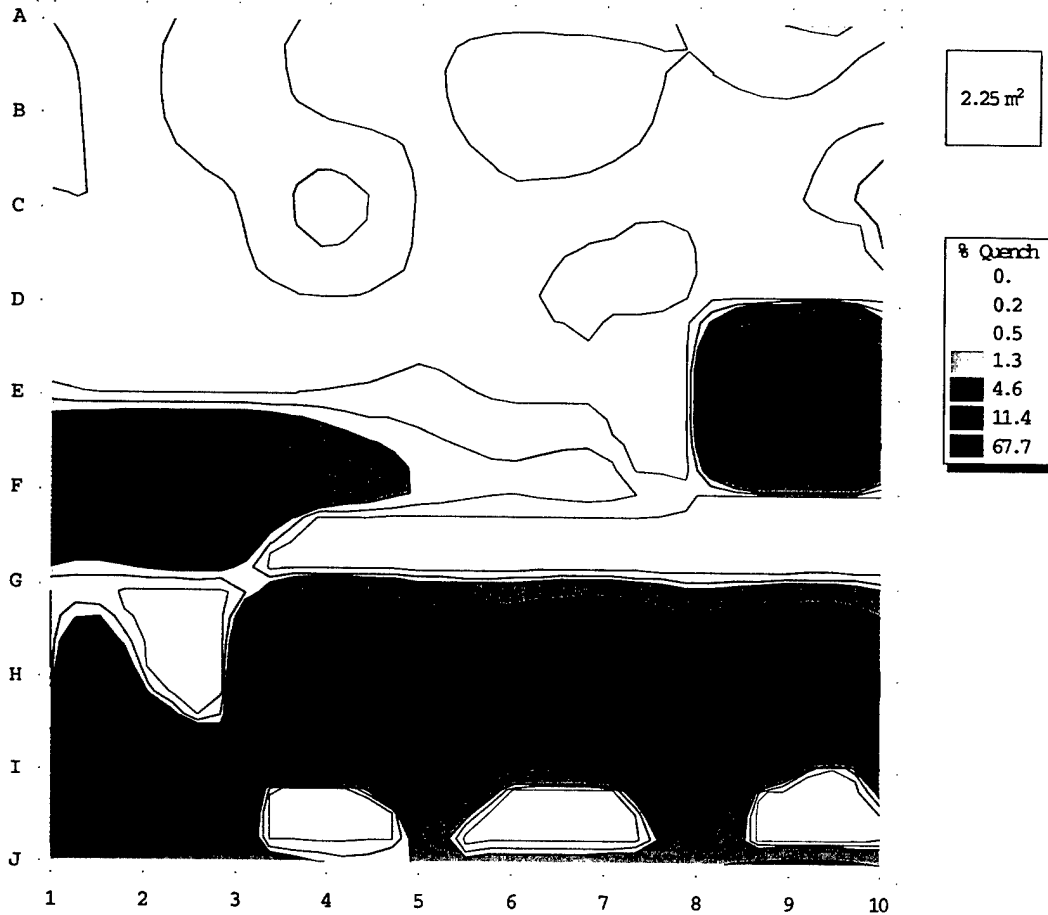
After all data had been presented for scoring, the ground truth for the site was made available. Once this information was available, it was possible to calculate the mean distance from a mine to its nearest neighbor in the lanes. Since Fido detects only TNT and explosives containing TNT (e.g., Composition B), mine types not containing TNT were excluded from the analysis. The mean spacing between mines in the lanes was approximately 3.8 meters. Hence, the average distance from any arbitrarily chosen point in the lanes to a mine is about half this distance, or a



**Figure 6. Sensor responses for samples collected perpendicular to mine lane.**

distance of approximately 1.9 meters. This value is almost identical to the detection radius of 1.75 meters measured for the samples collected perpendicular to a mine lane. Hence, the data strongly suggest that the chemical signatures of individual mines in these lanes are dispersed enough that they likely overlap.

Figure 7 is a Fido response contour map constructed for the square grid. The darker shading indicates a higher detected concentration of TNT, while lighter shading indicates a lesser concentration. The density of mines in this grid is also very high, so the probability of being near a mine anywhere in the grid is similar to that of the mine lanes. As a consequence of the high density of mines in the grid, a majority of the samples analyzed from this grid contained ERCs. While it is impossible to pinpoint the locations of mines from this data, if the ground truth is overlaid on this data, the positions with high TNT concentrations are in most cases very close to mined positions. It is apparent from the plot that the TNT plumes of adjacent mines frequently overlap.



**Figure 7. Contour map of Fido TNT response for square grid.**

The samples from the grid were collected over two days. Rows A-D were sampled at the end of the second day of testing, and the remaining rows were sampled the next morning. As previously mentioned, a light rain fell during the night before the third day of testing. The soil was wet early in the morning but quickly dried as the morning progressed. Note that the intensity of responses by Fido in general seemed to increase for samples collected after rain fell on the site. It could be argued that rain provided adequate soil moisture to enable transport of signature compounds from subsurface soils to the surface of the ground as the water evaporated the next morning. This would enhance soil explosive signature concentrations on surface soils, leading to stronger sensor responses.

Some studies with canines have suggested that the apparent radius of detection for mines is significantly greater than 2.0 meters [16]. Regardless, prior experimentation would seem to indicate that the distinction between individual mine “plumes” would require a mean inter-mine spacing in excess of at least 2.0 meters. The results of previous fieldwork by Nomadics and published results of the DARPA Explosive Fate and Transport Team (EF&T) also support this conclusion. Field data from tests at Ft. Leonard Wood indicate that landmine chemical



signatures frequently extend one meter or more from the mine centers [3, 6], adding validity to the assertion that the mine signatures at YPG may have overlapped significantly.

It should be noted that YPG was designed for testing metal detectors and other sensor technologies that do not utilize trace chemical detection. The test field at Ft. Leonard Wood contains areas of high mine density, but also contains areas where the distance between mines is in excess of 10 meters. The larger spacing was deliberate in the Ft. Leonard Wood field to reduce overlap of mine chemical signatures.

In summary, it is our conclusion that Fido was indeed detecting mine signatures at YPG, but the high density of mines in the lanes produced a situation in which the chemical signatures from the mines overlapped each other. This made it difficult to pinpoint the exact location of mines in the lanes with any degree of certainty. The data support the conclusion from previous field tests that mine signatures can extend a significant distance away from the center of a mine. Also important is the finding that areas away from mine locations produced few sensor responses, while sensor responses within mined areas (i.e., mine lanes) were frequent. Since few samples outside mine lanes gave a positive response, the notion that the sensor was generating false alarms inside the lanes is doubtful. The data also suggest that background contamination of the site was minimal, in spite of frequent detonations of munitions at the site. The findings suggest that trace chemical detectors for explosives may have utility for area reduction of suspected minefields.

### **3.2 *Sensor Conclusions***

Recent field and laboratory investigations of trace landmine chemical signatures suggest that the explosive chemical signature emanating from mines is not necessarily localized immediately over the mine but can extend a significant (but as of yet not well characterized) distance from the mine center. Hence, trace chemical detectors may not be very useful for pinpointing the exact location of mines but may be helpful for detecting dispersed landmine chemical signatures. These dispersed signatures may be indicative of the presence of minefields. More study is needed to determine the range and mechanism of dispersal of landmine signatures in the environment. A sensor capable of detecting these signatures has been demonstrated and is undergoing further development. However, in order to utilize these sensors to fullest advantage, new sampling paradigms are needed for efficient sampling of widely dispersed minefield chemical signatures.

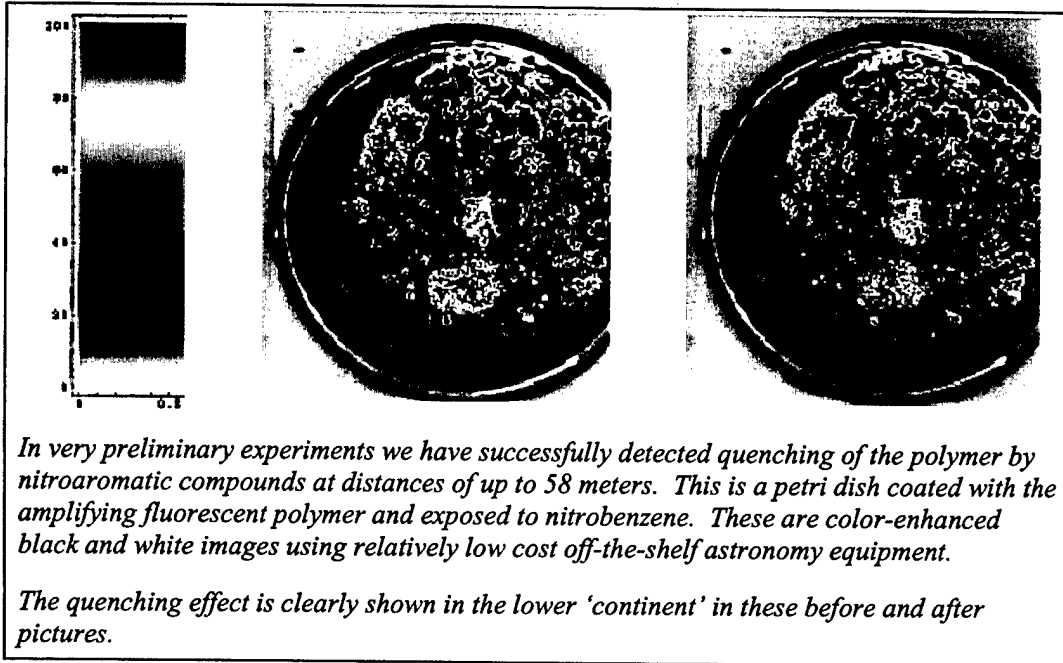
## **4. Standoff Landmine Detection Using Amplifying Fluorescent Polymers**

### **4.1 *Introduction***

Under a modification to this contract Nomadics investigated the feasibility of using the amplifying fluorescent polymer material in standoff landmine detection applications. Even when using an extremely sensitive sensor as the Nomadics detector, the vapor pressure of TNT is so low that 'sniffing' at any significant distance is extremely difficult. Consequently, our approach in this case is to deliver the polymer material in micro- or nanoparticle form and optically view the resultant quenching in the presence of TNT from a distance. This approach may have applications in both military and humanitarian landmine detection as well as naval force protection.

#### 4.2 Standoff Test Bed

Nomadics designed and assembled an optical test bed to try out various approaches. Using primarily off-the-shelf components, we have successfully demonstrated detection of quenching of amplifying fluorescent polymer coated on petri dishes and exposed to nitrobenzene at up to 58 meters (Figure 8).

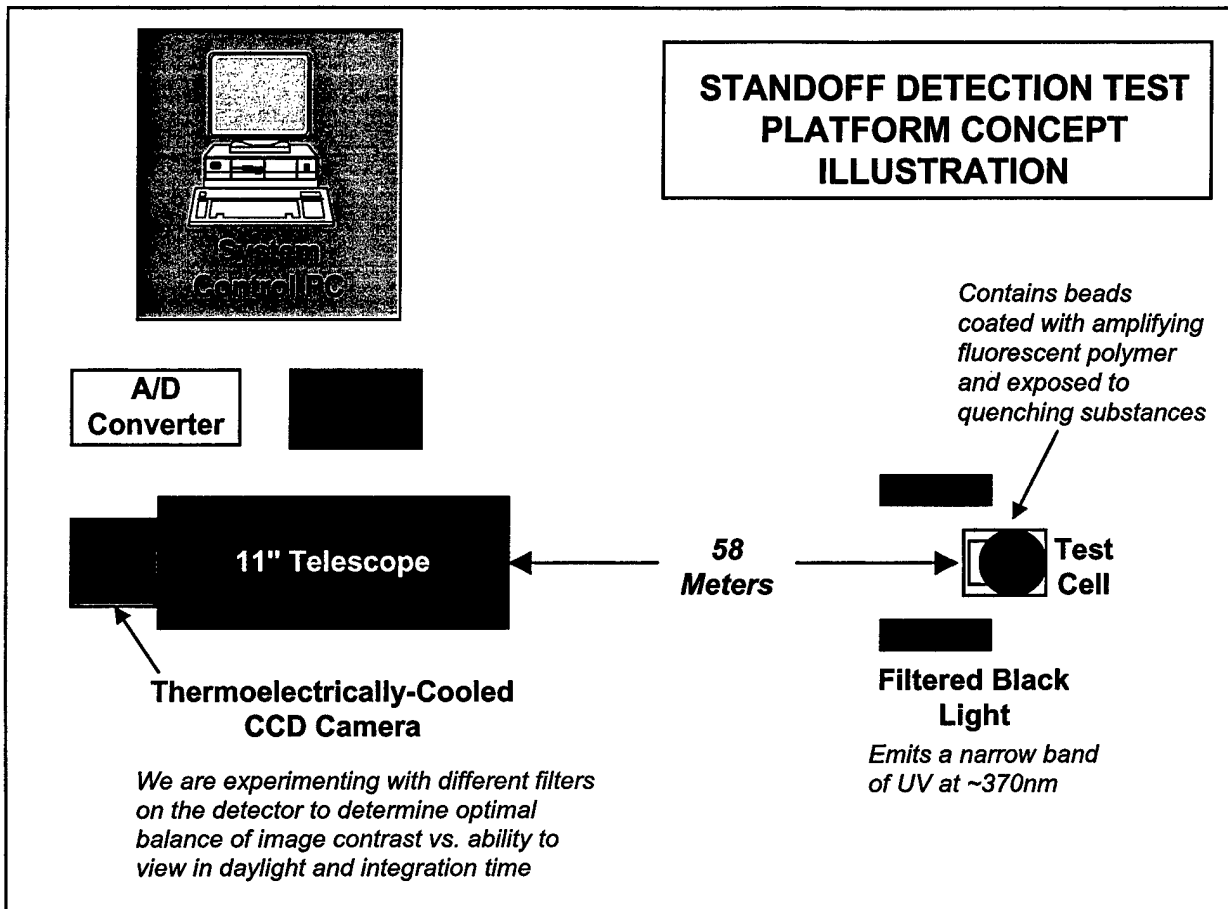


**Figure 8. Preliminary results showing detection of quenching from a distance.**

The major elements of the test bed include an 11" Celestron telescope, Liconix 10mW helium-cadmium laser, a thermoelectrically cooled astronomy camera with CCD element, an A/D assembly, and a system controller. The test bed is illustrated in Figures 9-11 below.



**Figure 9. Optical test bed photos**



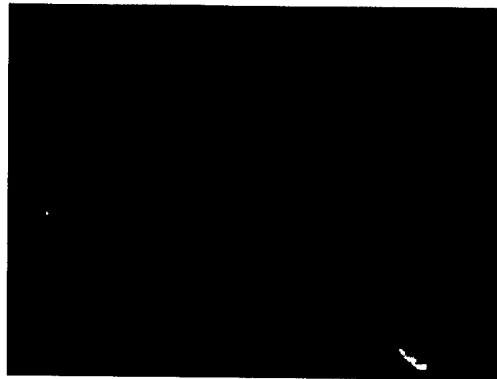
**Figure 10. Optical test bed system diagram.**

Tests were performed by coating micron size polystyrene-divinylbenzene beads with the polymer. Original tests used a 10 mW HeCd laser that outputs at 441.6 nm. This beam was either projected directly onto the test cell or was "spatially mixed" by injecting into a fiber optic cable and then focused onto the target. The spatial mixed beam has the advantage of a fairly uniform illumination rather than the Gaussian profile that comes directly from the laser. The disadvantage of using the fiberoptic as a mixer was reduction in power by about 20% and the resulting interference pattern would change if the fiber optic cable was moved. Initial tests at 58 meters were done with the HeCd laser actually being only one to two meters from the test cell. This was done in the interests of eye safety to other Nomadics employees. Later tests involved using black light fluorescent lamps that had been filtered with UG-1 Schott glass. This provided even lighting at higher intensities than could be achieved with the 10mW HeCd. This allowed us to concentrate on the proof of concept and the detection optics.

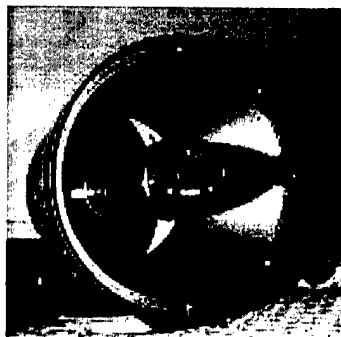
A CCD camera was used with the ship array being cooled by a two-stage thermoelectric cooler and water radiator. This permitted us to operate the camera at  $-25$  to  $-39^{\circ}$  C. This in turn drastically reduces the dark noise of the camera.



*Test cell with filtered backlight (non-illuminated)*



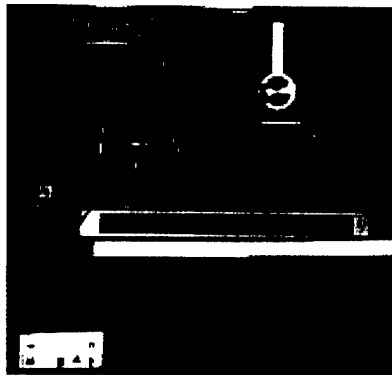
*Illuminated test cell showing fluorescing polymer-coated beads in test plate*



*11" Celestron telescope*



*CCD camera mounted on back of telescope*



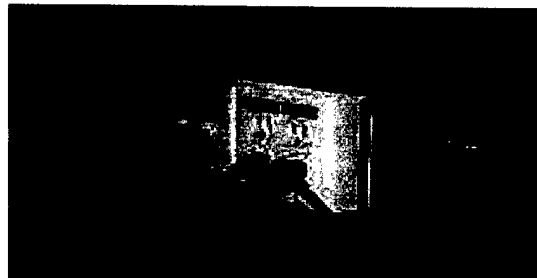
*Illumination table*



*System controller*



*AID converter*



*Power supply*

**Figure 11. Standoff detection system elements.**

The measurements were repeated after the introduction of nitrobenzene-contaminated samples through a septum in the test cell. Nitrobenzene was used because, as a nitroaromatic, it shares many of the chemical characteristics of TNT—including quenching of the polymer—while being easy to handle and clean up. The graph in Figure 12 shows the results of one test. The vertical axis represents change in the detection signal while the horizontal axis shows progression over time based on the frames of the CCD. With the introduction of sample at frame 2, an immediate response is evident. Interestingly, the outlying data point at frame 18 was the result of a person passing between the test cell and the telescope.

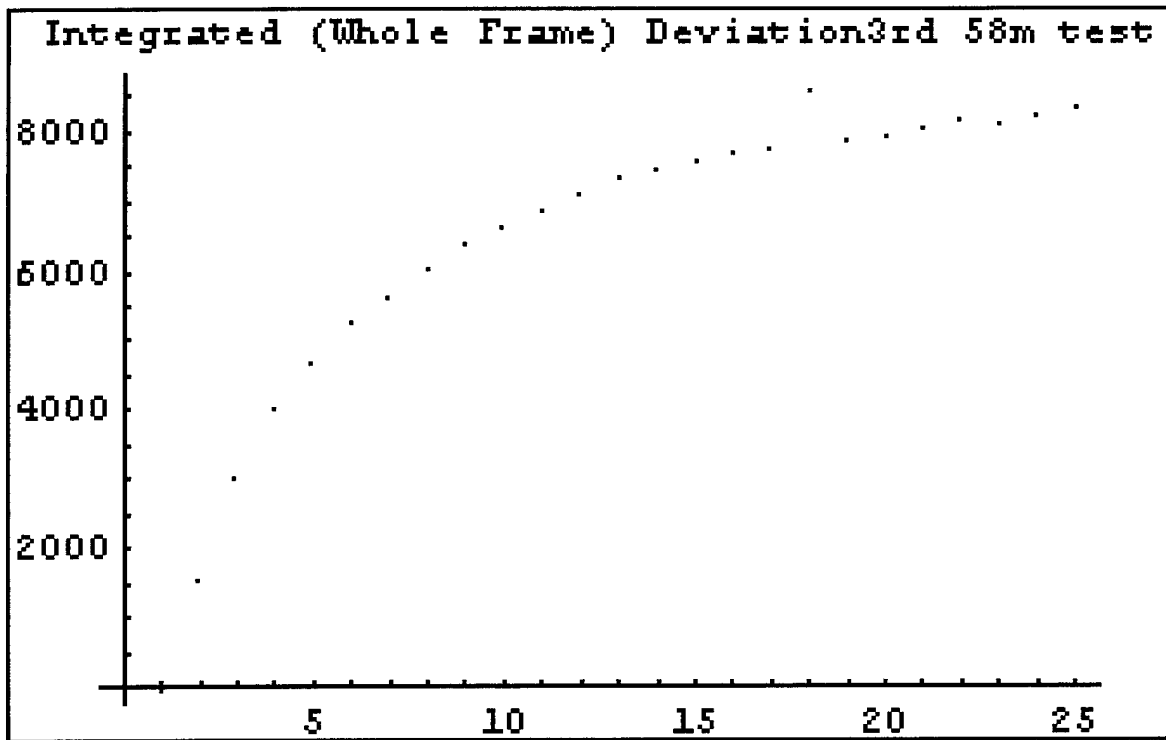


Figure 12. Standoff detection - results of introduction of contaminated samples.

#### 4.3 Standoff Detection Conclusions

These initial trials were extremely successful and promising. They have clearly shown that polymer-coated beads quench in the presence of explosive compounds. Future tests under other contracts will be conducted at longer distances and outdoors to determine the feasibility of deployment in field conditions.

This document reports research undertaken at the U.S. Army Soldier and Biological Chemical Command, Soldier Systems Center, and has been assigned No. NATICK/TR-03/010 in a series of reports approved for publication.

## References

1. V. George, Jenkins, T.F., Leggett, D.C., Cragin, J.H., Phelan, J., Oxley, J., and Pennington, J., "Progress on Determining the Vapor Signature of a Buried Landmine", Proc. SPIE, Detection and Remediation Technologies for Mines and Minelike Targets IV, vol. 3710, part 2, p. 258-269 (1999).
2. M.E. Walsh and T.F. Jenkins, "Identification of TNT Transformation Products in Soil", SR92-16, US Army Corps of Engineers, Cold Regions Research and Engineering Laboratory (1992).
3. T.F. Jenkins, M.E. Walsh, P.H. Miyares, J.A. Kopczynski, T.A. Ranney, V. George, J.C. Pennington, and T.E. Berry, "Analysis of Explosives-Related Signature Chemicals in Soil Samples Collected Near Buried Landmines", ERDC Technical Report 00-5 (2000).
4. J.M. Phelan, and S.W. Webb, "Environmental Fate and Transport of Chemical Signatures from Buried Landmines - Screening Model Formulation and Initial Simulations", Sandia Report SAND97-1426, Sandia National Laboratories (1997).
5. V. George, T.F. Jenkins, J.M. Phelan, D.C. Leggett, J. Oxley, S.W. Webb, P.H. Miyares, J.H. Cragin, J. Smith, T.E. Berry, "Progress on Determining the Vapor Signature of a Buried Landmine", Proc. SPIE, Detection and Remediation Technologies for Mines and Minelike Targets V, vol. 4038, part 1, p. 590 (2000).
6. A.D. Hewitt, T.F. Jenkins, and T.A. Ranney, "Field Gas Chromatography/Thermionic Detector System For On-Site Determination of Explosives In Soil", ERDC Technical Report 01-9, (2001).
7. J.M. Phelan, S.W. Webb, M. Gozdor, M. Cal, and J.L. Barnett, "Effect of Soil Wetting and Drying on DNT Vapor Flux – Laboratory Data and T2TNT Model Comparisons", Proc. SPIE, Detection and Remediation Technologies for Mines and Minelike Targets VI, vol. 4394, part 2, p. 868-878, (2001).
8. C. Cumming, C. Aker, M. Fisher, M. Fox, M. laGrone, D. Reust, M. Rockley, T. Swager, E. Towers, and V. Williams, "Using Novel Fluorescent Polymers as Sensory Materials for Above-Ground Sensing of Chemical Signature Compounds Emanating from Buried Landmines", IEEE Transactions on Geoscience and Remote Sensing, Vol. 39, No. 6, pp.1119-1128 (2001).
9. M. laGrone, C. Cumming, M. Fisher, M. Fox, S. Jacob, D. Reust, M. Rockley, and E. Towers, "Detection of Landmines by Amplified Fluorescence Quenching of Polymer Films: A Man Portable Chemical Sniffer for Detection of Ultratrace Concentrations of Explosives Emanating From Landmines", Proc. SPIE, Detection and Remediation Technologies for Mines and Minelike Targets V, vol. 4038, part 1, p. 553-562 (2000).
10. M. laGrone, C. Cumming, M. Fisher, D. Reust, and R. Taylor, "Landmine Detection By Chemical Signature: Detection of Vapors of Nitroaromatic Compounds by Fluorescence

Quenching of Novel Polymer Materials”, Proc. SPIE, Detection and Remediation Technologies for Mines and Minelike Targets IV, vol. 3710, part 1, p. 409-420 (1999).

11. J.S. Yang, and T.M. Swager, "Porous Shape Persistent Fluorescent Polymer Films: An Approach to TNT Sensory Materials," *J. Am. Chem. Soc.*, 120, 5321-5322 (1998).
12. J.S. Yang, and T.M. Swager, "Fluorescent Porous Polymer Films as TNT Chemosensors: Electronic and Structural Effects", *J. Am. Chem. Soc.*, 120, 11864-11873 (1998).
13. V. Williams, T.M. Swager, "Iptycene-Containing Poly(aryleneethynylene)s", *Macromolecules*, 33, 4069-4073 (2000).
14. Q. Zhou and T. Swager, "Methodology for Enhancing the Sensitivity of Fluorescent Chemosensors: Energy Migration in Conjugated Polymers", *J. Am. Chem. Soc.*, 117, p. 7017-7018 (1995).
15. *Jane's Mines and Mine Clearance*, Colin King ed., 1999-2000 (Fourth Edition).
16. R.V. Nolan and D.L. Gravitte, " Mine Detecting Canines", Report 2217, US Army Mobility Research and Development Command, 1977.