

Utilization of Chemical Vapor Detection of Explosives as a Means of Rapid Minefield Area Reduction

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Abstract

Clearing large areas that are suspected of containing landmines is an expensive and time-consuming task. Upon the completion of demining operations, few, if any, landmines may be found. Technologies that can locate individual landmines in a minefield exist, but most of these methods are relatively slow and expensive. In addition, these technologies are not generally suitable for rapid screening of an area for the presence of landmines. Hence, technologies that can quickly ascertain whether there is an actual landmine threat in an area are needed.

The explosive contained in landmines produces a bouquet of chemical vapors that can contaminate the environment near a mine. Under the DARPA Dog's Nose Program, Nomadics developed a sensor (known as Fido) that utilizes novel fluorescent polymers to detect ultra-trace concentrations of nitroaromatic compounds emanating from landmines. Evidence currently available indicates that it may be possible to quickly deduce mine locations to within an area of a few square meters. Field data supporting this conclusion have been obtained using our sensor, and the conclusions drawn are supported by other accepted laboratory analysis methods. These results are driving development of sampling and sensing equipment that may be suitable for rapidly isolating mined areas within large minefields. Preliminary data from field tests using prototype soil and vapor samplers with Fido sensors will be presented.

Keywords: landmines, UXO, explosives detection, chemical sensing, area reduction

I. 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 such as mine type, the condition of the mine casing, soil type, soil moisture content, burial depth, vegetation, and the 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. The 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 dispersal of signature has also been observed to be non-symmetrical and can be influenced by factors such as the soil topography near the mine [3, 6].

Thus, pinpointing the location of a mine using trace chemical sensors is difficult. However, trace chemical detection could be used to determine whether or not dispersed explosive signatures are present in an area, indicating that mines may be present. Once an area is deemed suspect, technologies that can pinpoint the exact location of the mines can be used. If successful, this area reduction technique will enable demining efforts to focus on areas that actually contain mines, rather than consuming significant resources in areas that are not mined.

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. The concentration of vapor phase TNT and ERCs in the air over 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 decrease.

Soil TNT concentrations at these levels can be detected by only a few laboratory instruments, such as a gas chromatograph (GC) utilizing an electron capture detector (ECD). Nomadics began developing an extremely sensitive detector for TNT (known as Fido) under the DARPA Dog's Nose Program [8–10]. Further development of the detection system is ongoing through funding by the US Army Night Vision and Electronic Sensors Directorate (NVESD). 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 laboratory sensors. Preliminary results from field tests of this system that demonstrate its possible use as a minefield area reduction tool will be presented.

II. OVERVIEW OF SYSTEM HARDWARE

A. 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 Fort Leonard Wood (FLW), Missouri, the sensor was able to detect TMA5 and PMA1A landmines. These field tests are described elsewhere [8–10]. Canines were also tested during these tests. The performance of Fido was comparable to that of the canines in this test [5].

Fido uses as sensory materials novel fluorescent polymers developed by collaborators at the Massachusetts Institute of Technology. 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 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. There is evidence that these polymers amplify the quenching response 100- to 1,000-fold as compared to conventional (monomeric) quenching mechanisms.

A schematic of Fido 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 response of the sensor 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.

B. Sampling Equipment

Field samples are collected by three methods. One method is direct sampling of vapor-phase analytes using the Fido sensor. 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 success of this sampling method is influenced 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. 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. 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 DARPA at the FLW test facility [8].

A second method of sampling is by use of an electrostatic soil particle collector (ESPC). The ESPC contains an electrically conductive cylinder that serves as an electrode. An air jet gently dislodges soil particles from the surface of the ground, while a pump draws air with entrained dust particles through the cylinder. A small diameter rod located on the axis of the cylinder serves as a second electrode. A corona is generated within the cylinder when a high voltage is applied across the electrodes. Soil particles drawn through the cylinder become highly charged and are attracted to the outer 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 then cleaned and reused. With this device it is possible to collect a sample of finely divided soil particles from over a relatively large area.

Another method samples both soil particles and vapor by drawing samples through a bed of vapor-adsorbent material. Soil particles are also trapped in the bed. Air is drawn at high flow rates through the adsorbent medium, enabling rapid sampling of large volumes of air and entrained particulates. After a sample is collected, the cartridge is removed, and any trapped analyte is extracted into solvent or thermally desorbed and presented to Fido via a portable GC.

C. Gas Chromatograph

A Fido sensor interfaced to a modified SRI Model 8610 gas chromatograph is currently being used to analyze soil particle samples collected with the ESPC and the high-volume sampling cartridges. The chromatographic retention data greatly improves system selectivity. The system can analyze a sample in under two minutes. Because of the sensor's selectivity, 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 viable for most minefield applications, the GC capability provided by this system is enabling collection of data that have proven extremely useful in developing an integrated sensor/high-volume sampling package. An integrated high-volume sampler and sensor is being designed using lessons learned from the chromatograph/sensor package.

III. FIELD TEST RESULTS

A. Fort Leonard Wood

Tests of the equipment previously described were conducted at Ft. Leonard Wood in October 2001. The test minefield contains a sensor calibration area where mines of known types are

buried at several depths. There are also several blind lanes in which antitank and antipersonnel mines are buried. Tests were conducted in both areas and on a number of targets selected by NVEDS, who directed the field tests. Final evaluation of the test results is pending.

Soil in vegetated areas was wet due to recent rains. Surface soils in areas where vegetation was absent were much drier, but subsurface soils in these areas were still wet. Surface air and soil temperatures were around 10-15° C for most of the test period, and winds were high.

High-volume vapor samples were collected over each position in two heavily vegetated blind lanes, as well as from an area with little vegetation where several mines were to be unearthed. Samples collected over unvegetated areas contained significantly more soil particulates than samples collected from the blind lanes, presumably due to the fact that surface soils in the unvegetated areas were much drier than soils in the blind lanes. The samples collected from the unvegetated areas often contained detectable ERCs, while samples from the vegetated blind lanes were all below detection limits of Fido. The fact that all the high-volume samples that tested positive for ERCs also contained a higher number of soil particles is probably significant.

Three high-volume vapor samples were taken for each mine that was unearthed. The first sample came from the surface soil before it was disturbed, the second from the bottom of the hole after the mine was removed, and the third from the soil removed from the hole. The samples from the bottom of the hole contained the highest average concentration of ERCs. The soil removed from the holes contained the second highest average concentration, while the surface soil samples showed the lowest concentrations.

The ESPC was not used during the FLW test due to the high soil moisture content. High-volume vapor samples, which normally contain a large number of soil particles, contained relatively few particles for the same reason. Because the soil was so wet, manually collected soil samples from each position in two blind lanes were obtained. Analysis of the samples by solvent extraction followed by GC/Fido analysis has been performed, along with GC/ECD analysis of the same samples. Surprisingly, almost all of the GC/Fido samples contained evidence of at least traces of TNT, as did many of the GC/ECD samples. It is not known at this time how the chromatographic results compare to the ground truth. If the contamination in the blind lanes turns out to be widespread, further investigation is warranted to determine the extent of chemical signature dispersion from mines in the field and also to investigate the mechanism of dispersal.

Spatial information relating to mine signatures has been collected at the FLW site on previous field trips by Nomadics and has been published by other investigators [3, 6]. Frequently, it has been observed that the signature is not confined to the immediate vicinity of the mine but can extend in a heterogeneous pattern to a significant distance away from the perimeter of the mine. The topography of the mine burial site is also important. For mines emplaced on a slope, signatures are frequently displaced in a direction downhill from the mine location. This is believed to be due to transport of the signature by runoff of water after rainfall.

B. Yuma Proving Grounds

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. YPG is 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 by 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. Both factors could be expected to reduce the surface concentrations of ERCs at Yuma. This proved to be the case with ERC concentrations below the detection limits of our laboratory GC with an ECD. However, Fido interfaced to the SRI 6890 was able to detect explosive signatures in many soil samples collected with the ESPC. Figure 3 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, which are 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.

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 during the night after the second day of testing, but the soil quickly dried the next morning. Soil particle samples taken on the days after the precipitation did show a trend of increasing ERC concentrations, but this increase was too modest to facilitate vapor phase sensing after the rain.

Particle samples were taken from an area, including five mine lanes, that was divided into 100 cells of 1.5 meters square. The samples were extracted into acetone and analyzed by GC/Fido. The chromatographic results were then submitted for independent analysis. By comparing the results using calibration standards, we came to believe that the system was capable of discriminating interferents from ERCs and detecting very low concentrations of explosives.

The initial test results were disappointing because explosive signatures in the soil within the lanes appeared to be widespread and not well correlated with mine locations, possibly due to widespread contamination of the site from the detonation of explosive devices and certain range management practices. To test this hypothesis, a follow-up trip was performed two months later.

When the soil samples from the second trip were analyzed, chemical signatures consistent with the presence of explosives were seldom detected away from the mine lanes. Of the 74 such “blank” samples, only 2 contained 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 other “blank” samples with detectable ERCs were observed. Soil samples were again taken from within some of the previously sampled mine lanes and were 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, refuting the hypothesis that the site was widely contaminated with ERCs.

Multiple samples were also collected along a line running perpendicular to the length of a mine lane. This line was selected so that it crossed over the top of a mine. Twelve samples were taken at +/- 2, 4, 6, 8, 10, and 12 feet north and south from the mine (Fig. 4). 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). By comparing this data to the ground truth for the site, 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, 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 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 5 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, 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.

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. Note that the intensity of responses seemed to increase for samples collected after rain fell, suggesting 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 suggest that the radius of detection for mines is significantly greater than 2 meters [16]. Fieldwork by Nomadics and published results of the DARPA Explosive Fate and Transport Team also support this conclusion. Field data from the FLW mine facility 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.

The YPG test facility was designed for testing metal detectors and other sensor technologies that do not utilize trace chemical detection. The test facility at FLW 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 FLW 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 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 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.

IV. 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 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.

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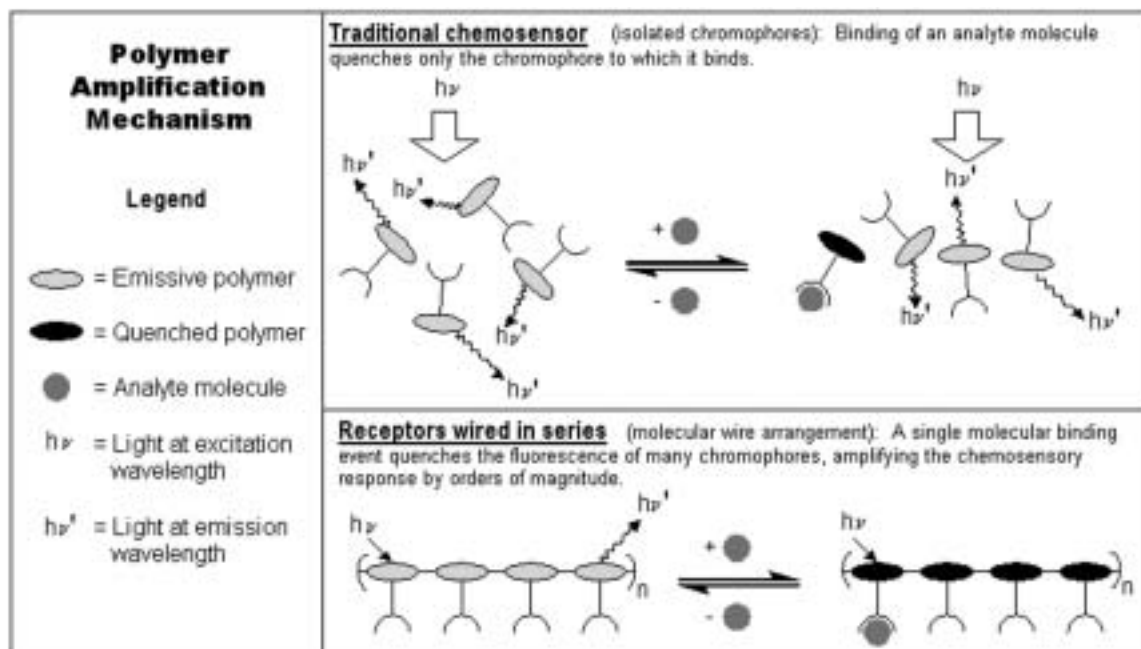


Fig. 1: Description of polymer quenching amplification mechanism.

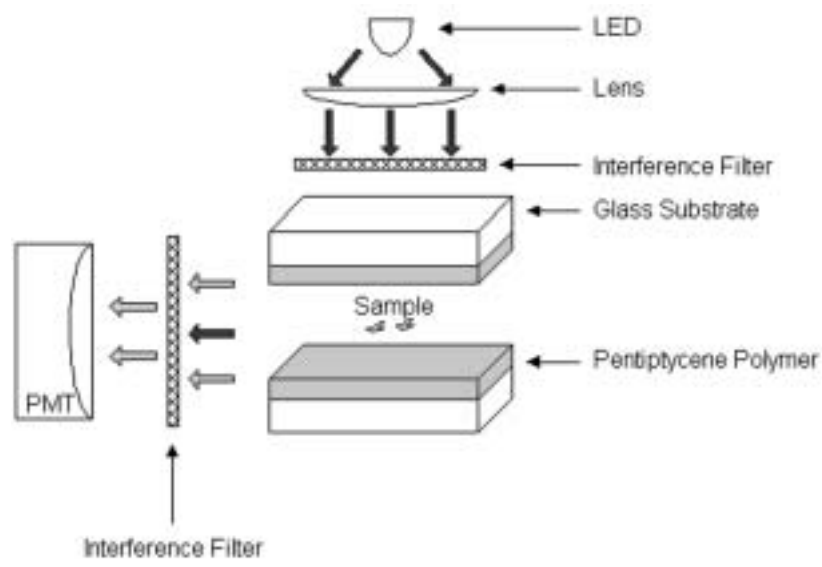


Fig. 2: A schematic of a Fido sensor prototype.

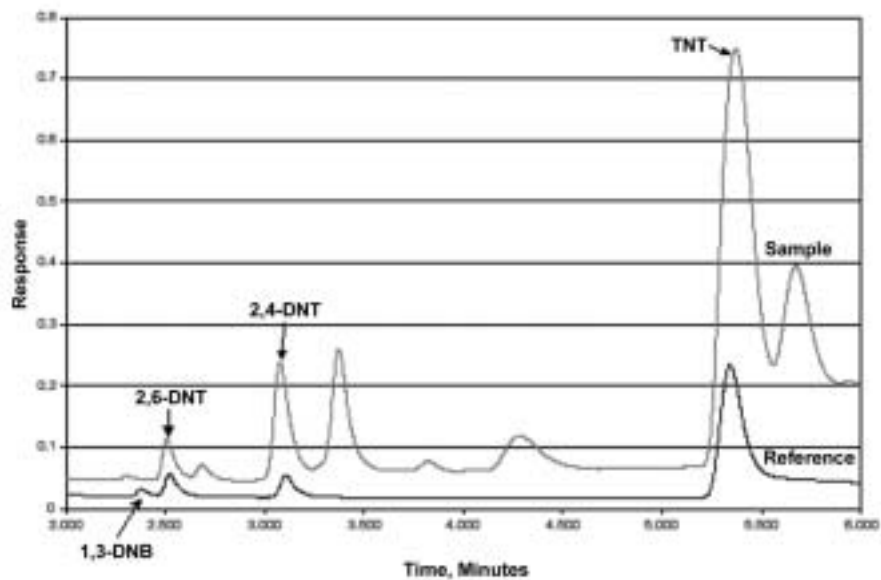


Fig. 3: Response of Fido to a 50-picogram reference standard mix and a soil particle extract collected over a TM62P3 landmine.

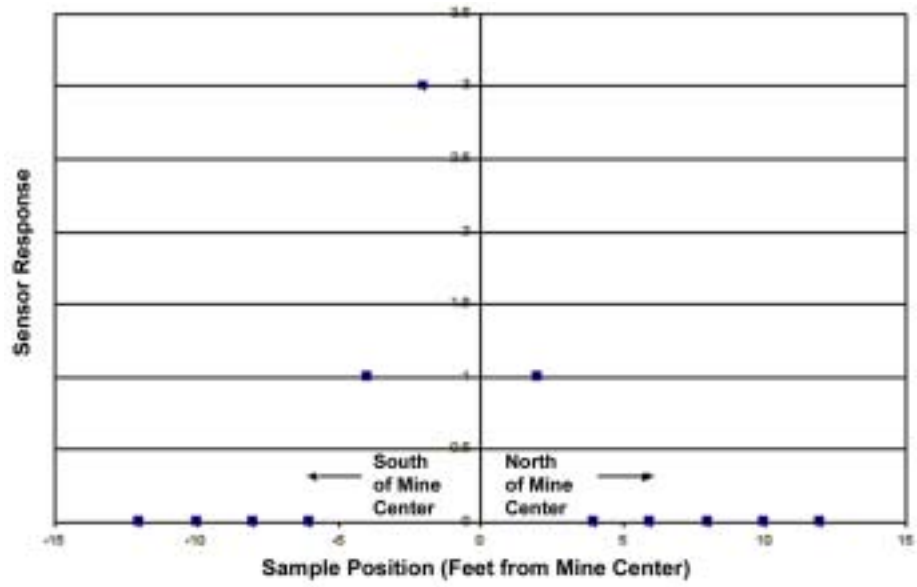


Fig. 4: Sensor responses for samples collected perpendicular to mine lane.

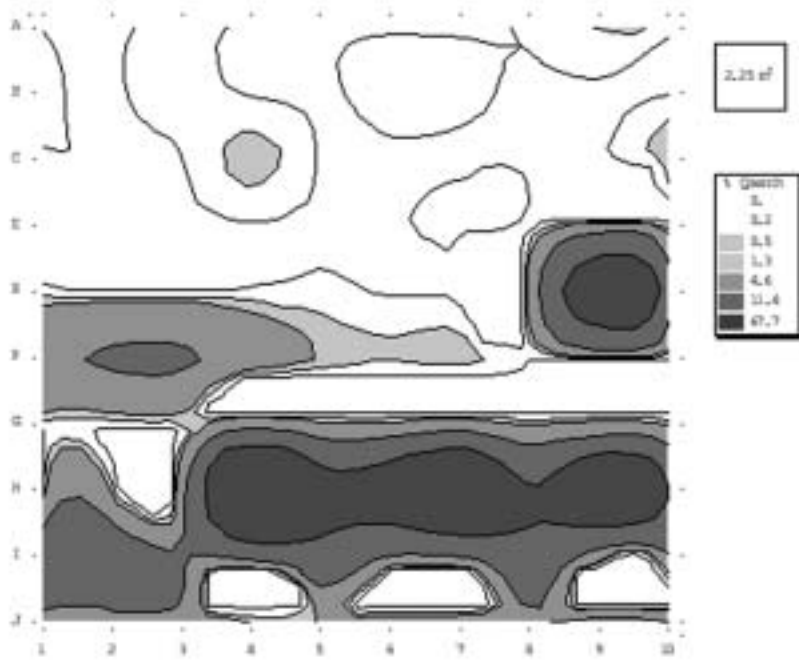


Fig. 5: Contour map of Fido TNT response for square grid.