# Using Novel Fluorescent Polymers as Sensory Materials for Above-Ground Sensing of Chemical Signature Compounds Emanating from Buried Landmines

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*Abstract*—Chemical vapors originating from the explosive charge within landmines and unexploded ordnance (UXO) form a chemical "signature" unique to these devices. The fact that canines can detect this signature was a primary motivation for the Defense Advanced Research Projects Agency's (DARPA) Dog's Nose Program. One goal of this program was to develop electronic chemical sensors that mimic the canine's ability to detect landmines. The sensor described here, developed under this program, utilizes novel fluorescent polymers to detect landmine signature vapors in air at ultratrace concentration levels (parts-per-trillion or less). Thin films of the polymers are highly emissive but undergo a dramatic reduction in emission intensity when molecules of target analytes bind to the polymer. Binding of a single explosive molecule can quench the fluorescence from hundreds of polymer repeat units, resulting in an amplification of the quenching response. The polymer structure contains receptor sites designed to interact specifically with nitroaromatic explosives, enhancing the selectivity of the polymers for target analytes. A man-portable sensor prototype, similar in size and configuration to metal detectors currently used for mine detection, has demonstrated performance comparable to that of canines during field tests monitored by DARPA at Fort Leonard Wood, MO.

*Index Terms*—Chemical sensing, explosives detection, fluorescence quenching, landmines, UXO.

## I. INTRODUCTION

THE WORLDWIDE landmine problem is one of astounding proportions. While it is difficult to determine the exact number of mines deployed worldwide, it is estimated that 60 to 70 million mines are deployed in approximately 70 countries. It has been estimated by the International Committee of the Red Cross that 26 000 people are involved in landmine incidents each year. Of this number, approximately 40% are children. Based on these statistics, a person is maimed or killed by a mine every 20 min [1]. In addition to the physical

and mental trauma inflicted by landmines, the effect on the economy of mined areas is devastating.

The time and cost involved in clearing a minefield and the danger faced by deminers in the process is enormous. The arsenal of mine detection equipment and techniques currently available to deminers is extremely limited, further compounding the problem. Currently, deminers and dismounted countermine engineers most frequently use metal detectors and probes to locate mines. Many modern landmines have very low metal content, severely limiting the effectiveness of metal detectors. "Probing" is an extremely dangerous and time-consuming method of detecting landmines. This method involves "feeling" for mines by methodically inserting rigid rods into the soil. When a solid object is encountered in the soil, it is then excavated to determine if the object is a mine. Canines have also been used for landmine detection for decades [2]. Even though canines can be effective for this purpose, their use is not without problems [3]. Logistical problems are significant, and dogs are expensive to train and maintain. Dogs do not perform well under all field conditions. In addition, the performance of the dog can be limited by the skill of the dog handler, the dog's desire to work, and the health of the dog. More technically advanced equipment such as ground penetrating radar (GPR) is currently included in the U.S. Army Handheld Standoff Mine Detection System (HSTAMIDS), but this system is not currently used in demining or countermine operations. Infrared sensing has also been investigated, but hand-held infrared detectors suitable for off-road use have not been developed. A single solution to the problem does not exist, and new mine detection technologies are desperately needed.

A serious limitation of landmine detection equipment currently in use is that of false alarms. Reducing the false alarm rates of this equipment has been extremely challenging. For example, mines with metal cases are relatively easy to detect with metal detectors. However, many modern mine cases are constructed of plastic, and metallic content is limited to fuze components. In order to detect these low-metal content mines, metal detectors with extremely high sensitivity are required. In mined areas, metallic objects such as shrapnel from previously exploded munitions and spent ammunition cartridges are commonly present in the soil. Under these conditions, it is difficult to distinguish low-metal content mines from other metallic objects in the soil. Since each potential target

identified must be treated as a mine until otherwise determined, a high false alarm rate is a serious limitation of any landmine sensing technology. Hence, high sensitivity and the ability to discriminate targets from clutter is essential. Unfortunately, it is difficult to achieve high sensitivity without a corresponding increase in the false alarm rate.

With the possible exception of canines, false alarms are due to the fact that currently available landmine detection technologies detect materials not unique to landmines. In an effort to address the false alarm problem, the focus of the DARPA Dog's Nose Program was to develop sensors that detect a material unique to landmines: the explosive. This program was inspired by the extraordinary ability of canines to detect the explosive charge present in landmines. The sensor system described here was one of several developed under this program. Our sensor detects vapors of nitroaromatic compounds derived from the parent explosive most commonly used in landmines (2,4,6-trinitrotoluene, or TNT). The sensor can detect low to subfemtogram masses of TNT without sample preconcentration. The fluorescent polymers utilized in the sensor respond to a limited subset of chemical compounds (primarily small, highly electron-deficient aromatic compounds with large reduction potentials). Fortunately, most compounds found in the environment do not fall into this category. Hence, the sensor responds preferentially to target analytes, with relatively few responses from potential chemical interferents.

## II. OVERVIEW OF CHEMICAL VAPOR DETECTION OF LANDMINES

### A. Landmine Chemical Signature Compounds

Almost 80% of the types of mines manufactured worldwide contain TNT, or mixtures of explosives containing TNT [4]. It is estimated that TNT-containing mines account for about 85% of the total number of landmines manufactured and hence now deployed. The mass of TNT contained in these mines ranges from as little as 7 g in a Canadian-manufactured C3A1 antipersonnel (AP) mine to as much as 13 kg in an Egyptian FBM antitank (AT) mine [4], [5]. Of the mine types that contain TNT, approximately 86% contain at least 50 g of TNT [5]. This mass of TNT is adequate to produce vapors of signature compounds that can be released into the soil for decades.

Military grade TNT is manufactured by the nitration of toluene [6]. This process produces many nitroaromatic compounds, some of which may remain in the TNT as contaminants at up to several percent by mass [7]. Some of these explosive-related compounds (ERCs) are significant contributors to the chemical fingerprint of a landmine [8], [9]. Of the ERCs found in TNT, those that are most prevalent in the vapor phase chemical signature of landmines include 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 1,3-dinitrobenzene (1,3-DNB), and 1,3,5-trinitrobenzene (1,3,5-TNB) [8]. The chemical structures of some of these compounds are shown in Fig. 1.

The equilibrium vapor concentration of TNT is very low (70 picograms /mL of air at 298 K) [6]. However, several of the contaminants present in TNT have higher equilibrium vapor pressures than TNT. Because their vapor pressures are higher, the concentration of these contaminants in the vapor phase signature may be orders of magnitude larger than that of TNT even though there
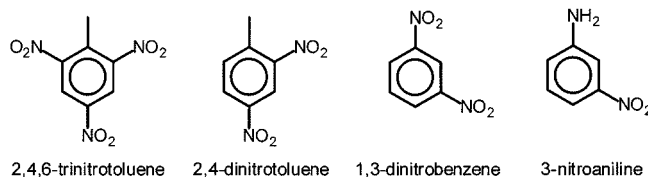


Fig. 1. Structures of some important landmine chemical signature compounds.

is much more TNT in the explosive charge. For example, analysis of TNT from a PMA-1A landmine found the headspace concentration of 2,4-DNT to be 20 times that of TNT even though the 2,4-DNT accounted for less than 1% of the explosive by mass [8]. 2,4-DNT is also more stable in the environment [10], and canines detect the 2,4-DNT found in TNT. For this reason, 2,4-DNT is the analyte of choice for vapor sensing of landmines.

In the environment, TNT and DNT both degrade. In addition to being a contaminant in TNT, 1,3,5-TNB is a photochemical degradation product of TNT. 2-amino-4,6-dinitrotoluene, and 4-amino-2,6-dinitrotolune are microbial degradation products of TNT [10]. The amino-DNTs have vapor pressures that are extremely low and hence are of little use for vapor sensing. However, they are frequently found in the soil over landmines, particularly during warm weather when microbial activity is high. Detection of other transformation products such as 3-nitroaniline, a microbial degradation product of 1,3-DNB, has been reported in the literature. While 2,4-DNT is the most likely analyte to be detected in the vapor phase [8], [9], any of these compounds signal the presence of TNT and hence, a landmine. It is therefore advantageous for chemical sensors to detect all of these compounds.

### B. Release of Signature Compounds from Mine Casings into Soil

Signature compounds are released into the surrounding soil through surface contamination of landmine cases, by vapor phase diffusion of analyte through the mine structural materials, and by leakage through cracks, seams, and holes in the mine. The latter two release mechanisms are the primary long-term release mechanisms. Surface contamination on the mine at the time of burial is quickly dispersed into the soil matrix surrounding the mine. Surface contamination on a plastic-cased Yugoslavian PMA-1A AP mine was measured and reported in the literature [8]. The surface of the mine was contaminated with 1,3-DNB, 2,4-DNT, and TNT. The total mass of these analytes distributed over the entire surface of the mine was 6.5 micrograms. This mass of analyte is insufficient to sustain long-term release of signature compounds into the soil. The total vapor-phase flux of signature compounds from several types of landmine cases was also measured in this study. The flux in this case was the total flux due to diffusion through structural materials and leakage through cracks and holes. The flux was measured into air and into water. For the PVC-cased PMA-1A landmine, the vapor-phase flux of 2,4-DNT into air was 3.4 micrograms per mine per day at 296 Kelvin, while the flux for the less volatile TNT was only 0.3 micrograms per mine per day. The flux rates into water were larger because of more favorable partitioning of ERCs into water than into
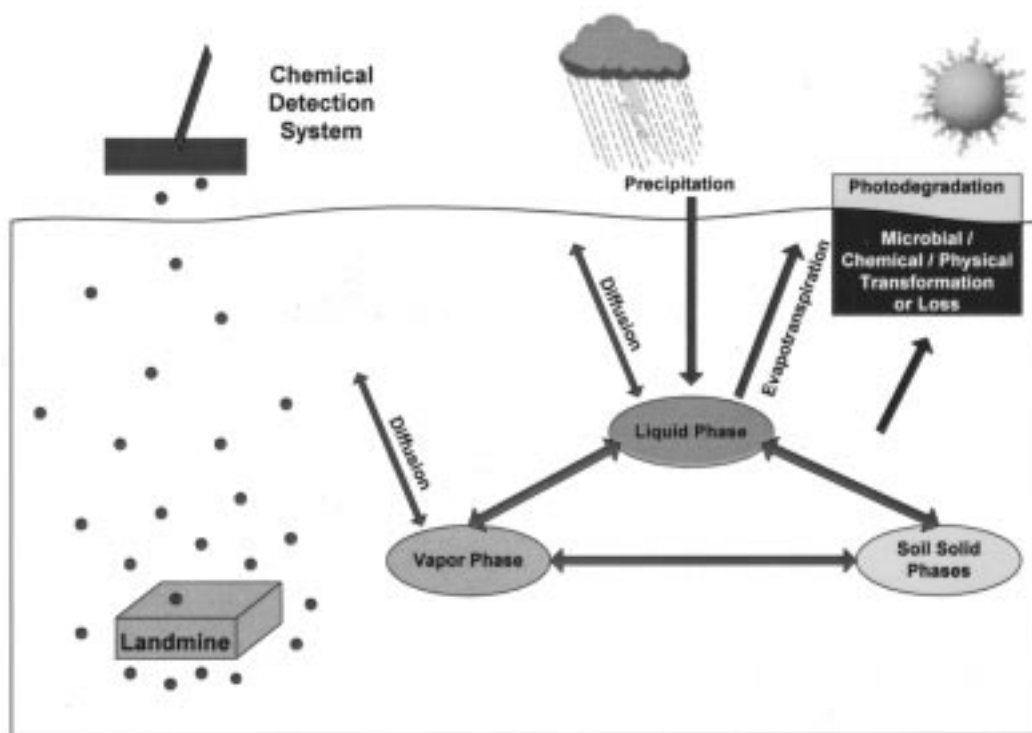
Fig. 2.   Processes affecting the fate and transport of landmine signature compounds in soil.

air. The flux rate of 2,4-DNT from a polystyrene-cased PMA2 AP mine into water was a factor of 30 larger than into air, and for TNT was a factor of 400 larger. It was estimated that the flux rate into wet soil would be intermediate between the air and water values. This has important implications for sensing mines since soil moisture content will strongly influence the rate of release of ERCs from mines. Note that of the mass of analyte released into the soil from the mine per day, only a small fraction will eventually reach the surface of the ground due to loss mechanisms described in Section II-C.

The vapor phase flux through a mine case varies depending on the type of material the mine is constructed from, and the structural design of the mine [8], [9]. Depending on the type of plastic used, flux rates from plastic-cased mines are typically higher than from metal cased mines. For a metal-cased Yugoslavian TMM-1 AT mine, the flux rate for 2,4-DNT is 2.3 $\mu$g/mine/day at 296 K. This compares with 3.4 $\mu$g per mine per day for the plastic-cased PMA-1A whose total surface area is approximately 6.5 times smaller than that of the TMM-1. Release of ERCs through intact metal-cased mines is presumably through seams, seals, and other nonmetallic structural materials. Flux rates are also somewhat temperature dependent, with the TNT flux rate from a PMA-1A increasing by a factor of 36 over a 31° temperature range spanning 276 K to 307 K.

### C. Fate and Transport of Signature Compounds in Soil

Fig. 2 illustrates some of the processes that occur in the soil near a buried landmine. Vapors of signature compounds escaping from the mine are quickly adsorbed onto soil solids or dissolve in soil water. Molecules of explosives such as TNT are strongly adsorbed by most surfaces. Due to the large surface area presented by soil particles and because of the adsorptive properties of explosives to solid surfaces [11], the majority of the ERC partitions onto the soil particles immediately surrounding the buried mine. The partitioning of ERCs into liquid and gas phases is governed by partition coefficients that are primarily a function of soil moisture content, and secondarily, a function of temperature and soil type [8], [9]. For a typical soil, approximately 95% of the total mass of ERCs is adsorbed onto soil solids, followed by approximately 5% into soil water, with a trace (approximately $1 \times 10^{-6}$%) partitioning into the vapor phase [12]. ERC accessibility and accumulation are further limited by irreversible binding to soil solids and by processes such as microbial degradation [10]. The half-life of TNT in certain soils when the conditions for microbial degradation are favorable is short, on the order of a few days [13], while 2,4-DNT is much more stable in the environment.

The primary mode of transport of ERCs to the soil surface is through the movement of water in the soil, not by molecular diffusion [12], [14]. Precipitation tends to draw ERCs downward through the soil. Conversely, water evaporating from the surface of the ground brings contaminated subsurface water to the surface (evapotranspiration). As the water evaporates, it deposits the semivolatile signature compounds preferentially on the comparatively drier soil particles at the surface of the ground. This behavior has also been observed for the transport of low-volatility pesticides whose chemical properties are similar to explosives [15]. Molecules of signature compounds then escape from contaminated soil particles at the surface of the ground and into the boundary layer of air near the surface of the ground. The concentration of ERCs in the boundary layer of air depends on the solid to vapor partition coefficient which is, as previously described, a function of soil moisture

content, temperature, and soil type. Photochemical degradation of some analytes may occur in soil exposed to sunlight. Some of these products, such as 1,3,5-TNB, are more volatile than the parent compound and escape from the soil more readily. These more transient compounds may not offer the consistent signature needed for reliable vapor detection. Analysis of numerous surface soil samples from the Fort Leonard Wood minefield have revealed the presence of 20 different ERCs in the soil near mines. However, three of these compounds (2,4-DNT, 4-amino-2,6-DNT, and 2-amino-4,6-DNT) are found much more frequently than the other compounds [9], [16]. Of these three, only 2,4-DNT is a realistic candidate for vapor-phase sensing due to the extremely low vapor pressure of the amino-DNTs.

In order for above-ground sensing of landmine chemical signature vapors to be viable, detectable concentrations of ERCs must be present in the air over a mine. It could be argued that for this to occur, the topmost layer of soil at the surface of the ground must be contaminated with ERCs. In order for surface soils to become contaminated, ERCs must escape from the mine into the soil in direct contact with the mine, and then the ERCs must be transported to the surface of the ground. The fate and transport of ERCs released into the soil from buried landmines has been the focus of a number of recent experimental and theoretical studies [8], [9], [12], [14]. These studies are beginning to reveal the conditions necessary to produce vapor concentrations of ERCs at the surface of the ground sufficient for mine detection using our sensor.

Perhaps the best evidence that landmine detection by vapor sensing is a feasible approach is that dogs can detect landmines under favorable conditions [3]. The canine olfactory system is an extremely sensitive chemical sensor. Elaborate experiments have been conducted that place the minimum detection limit for canines sensing explosives and ERCs in the low parts-per-trillion range [17]. These dogs are specifically and rigorously trained to detect the chemical signature of explosives, not the structural materials that make up the mine.

Experiments in the laboratory have shown that the concentration of ERCs in the headspace over trace contaminated soils is heavily dependent on soil moisture content [9]. For a given soil contaminated with ERCs, the concentration of ERCs in the headspace over the soil can span five orders of magnitude as a function of soil moisture content. Hence, the water content of surface soils is a very important consideration when sampling vapor phase ERCs to locate landmines. Experts have estimated the concentration of ERCs present in the air over landmines by assuming ERCs sorbed on soil particles and ERCs in the vapor phase can attain equilibrium in the thin boundary layer of air near the ground. These estimates put the concentration of TNT present in the air over a landmine at three to six orders of magnitude below its equilibrium vapor concentration [12], [14]. This places the concentration of TNT in the air over a landmine in the parts-per-trillion (ppt) to parts-per-quadrillion (ppq) range. In terms of mass of analyte per milliliter of air, the concentrations range from femtograms ($10^{-15}$g) to low attograms ($10^{-18}$g) per ml of air. These concentrations are well below the detection limits of field-transportable chemical vapor sensors currently available [6].

## III. USE OF AMPLIFYING FLUORESCENT POLYMERS AS SENSORY MATERIALS

### A. Amplification Mechanism

Based on the reasons discussed in Section II, we targeted TNT and 2,4-DNT as the most likely compounds for reliable vapor-phase detection of landmines. In order to achieve the extreme sensitivity for detection of landmines via vapor sensing of TNT and 2,4-DNT, novel fluorescent polymers were specifically engineered for TNT detection [18]–[20]. Conventional fluorescence detection normally measures an increase or decrease in fluorescence intensity, or an emission wavelength shift that occurs when a single molecule of analyte interacts with a single fluorophore. The upper right frame of Fig. 3 illustrates a transduction mechanism of this type.

In order to amplify the signal produced by a single TNT molecule, we sought to link individual fluorescent monomers forming a conjugated polymer. When a polymer molecule with a conjugated backbone absorbs a photon of light, the backbone of the polymer can act as a "molecular wire," enabling the propagation of the excitation along the polymer backbone [21]. The exciton (excited state electron) propagation distance is determined by the migration rate of the exciton and the lifetime of the excited state. If either the rate of migration of the exciton or its excited state lifetime is large, the exciton may sample many receptor sites during its lifetime. Eventually, the exciton will transition back to the ground state. Some of the transitions back to the ground state may result in fluorescence. The number of excitation events resulting in fluorescence is given by the expression

$$n = I_a \phi_f$$

where

$n$     number of adsorption events that result in fluorescence;

$I_a$     number of light quanta absorbed;

$\phi_f$     fluorescence quantum efficiency.

When an electron-deficient (i.e., electron accepting) molecule such as TNT binds to a receptor site, 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 nonradiative process) and no fluorescence will be observed from the excitation event. In effect, since the exciton samples many receptor sites, the probability that the exciton will sample an occupied receptor site is greatly increased. Hence, the probability that a photon absorption event will result in fluorescence is greatly reduced when TNT molecules are present, resulting in an amplification of the quenching response (refer to lower frame of Fig. 3). For simplicity, assume that the migration of the exciton is confined to a single polymer chain. If the exciton samples every receptor site in the entire polymer chain consisting of $N$ repeat units before transitioning back to the ground state, binding of a single analyte molecule to the chain results in quenching of $N$ repeat units. By comparison, if the entire polymer chain consisting of N repeat units were broken into $N$ monomeric units, one binding event would quench only one of the repeat units, resulting in a reduction in emission of only $1/N$. The amplification effect described
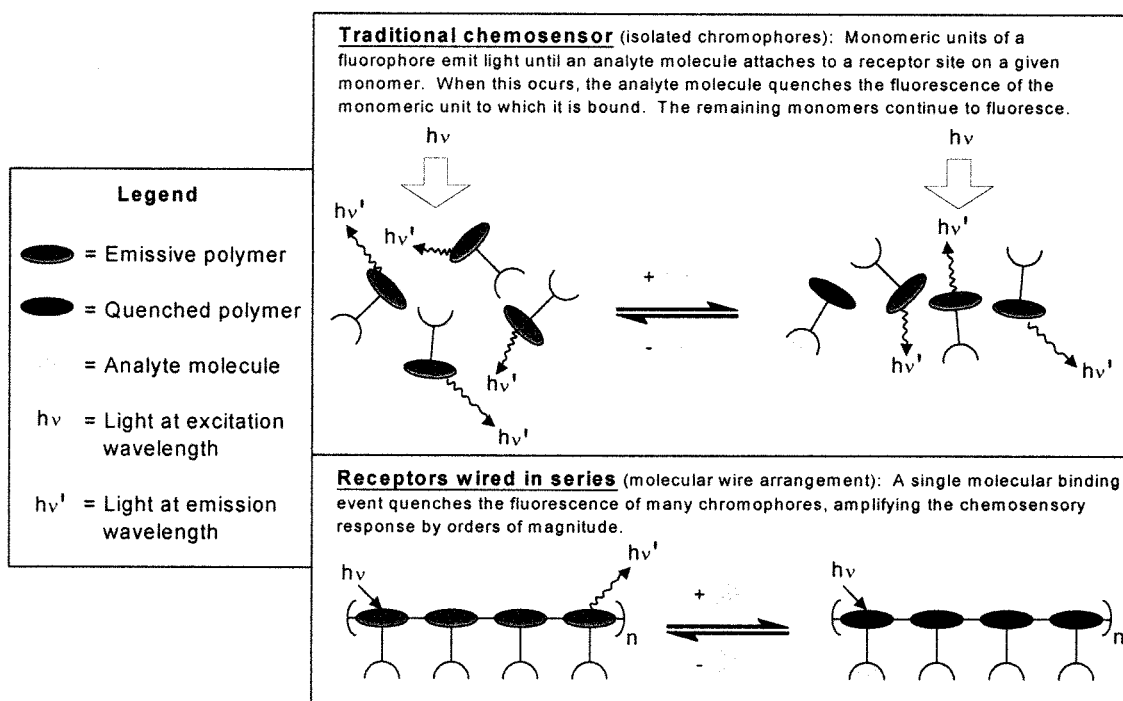
**Legend**

⬭ = Emissive polymer

⬬ = Quenched polymer

⌣ = Analyte molecule

hν = Light at excitation wavelength

hν' = Light at emission wavelength

**Traditional chemosensor** (isolated chromophores): Monomeric units of a fluorophore emit light until an analyte molecule attaches to a receptor site on a given monomer. When this ocurs, the analyte molecule quenches the fluorescence of the monomeric unit to which it is bound. The remaining monomers continue to fluoresce.

**Receptors wired in series** (molecular wire arrangement): A single molecular binding event quenches the fluorescence of many chromophores, amplifying the chemosensory response by orders of magnitude.

Fig. 3. Comparison of flouresence quenching for isolated chromophores with that of chromophores connected in a "molecular wire" configuration.

here is the mechanism responsible for the exceptional sensitivity of the sensor. In practice we believe our polymers produce an amplification of between 100 and 1000 as compared to conventional (monomeric) quenching mechanisms.

### B. Engineering Selectivity into Polymer Materials

Thin films of these materials coated onto a suitable substrate form the sensory element of our detection system. These films exhibit high fluorescence and spectroscopic reproducibility. Structurally, our polymers consist of a conjugated backbone with rigid, three-dimensional (3-D) pentiptycene groups. These structural entities minimize undesirable self-quenching that results from overlap of the backbones of the highly conjugated polymer chains ($\pi$-stacking) [19]. The rigidity and 3-D structure of the polymer forms cavities in the films that accommodate small molecules and help to enhance diffusion of small molecules into the films.

These polymers are engineered to be preferentially responsive to specific target analytes via three mechanisms. The first of these mechanisms is through steric constraints. Small molecules such as the target ERCs fit into the cavities in the films, while larger molecules are excluded [18]. The second mechanism providing selectivity is electrostatic complementarity between the polymer and target analytes. It is postulated that the polymers, which are electron-rich, bind reversibly to electron-deficient nitroaromatics through an electrostatic-type interaction. Receptor sites are specifically synthesized to be electrostatic mirror-images of the target analytes. This further increases selectivity via enhanced electrostatic interaction between the polymer and target ERCs. Fig. 4 shows the electrostatic surface of one of the polymers utilized in the sensor and that of a TNT molecule to illustrate the complementary nature of the electrostatic surfaces.

Finally, additional selectivity is attained by matching the reduction potential of the analyte and the effective ionization energies of the polymer. These factors are important since the ability to form an energy trap is defined by the strength of the binding complex formed between the polymer and the analyte.

## IV. INSTRUMENT OVERVIEW

### A. Sensor Architecture

When molecules of nitroaromatics bind to the polymers, the intensity of the fluorescence is greatly reduced due to the amplifying effect of the polymer. This reduction is proportional to the mass of quencher adsorbed by the films and is measured by the sensor system, hereafter referred to as FIDO. A schematic of FIDO is shown in Fig. 5. A blue light emitting diode (LED) serves as the fluorescence excitation source. Light from the LED passes through a lens that focuses the beam and directs it onto an interference filter that passes a narrow band of light centered at the excitation wavelength, ca. 370 nm. The filtered light then passes at normal incidence through two borosilicate 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. A significant fraction of the fluorescence couples into the substrates and is waveguided to the edges of the substrates. Additional light is reflected back into the waveguide paths by reflective coatings on three edges of the substrate. Emitted light is detected by a small photomultiplier tube (PMT) or avalanche photodiode.

### B. Sensor Operation

A sampling cycle begins by establishing a baseline fluorescence reading in clean air (i.e., air free of nitroaromatics). Air
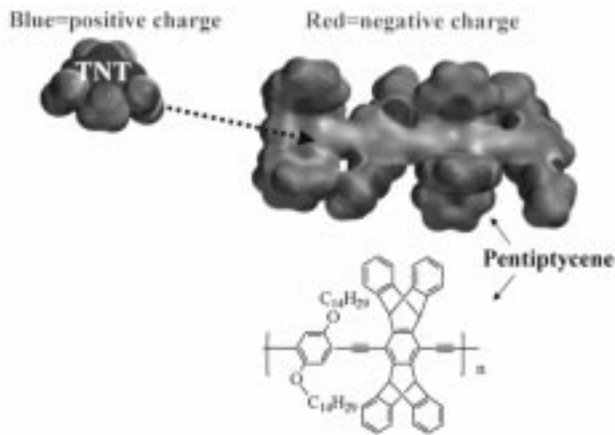
Fig. 4.   Electrostatic surfaces of an amplifying polymer and a molecule of TNT.
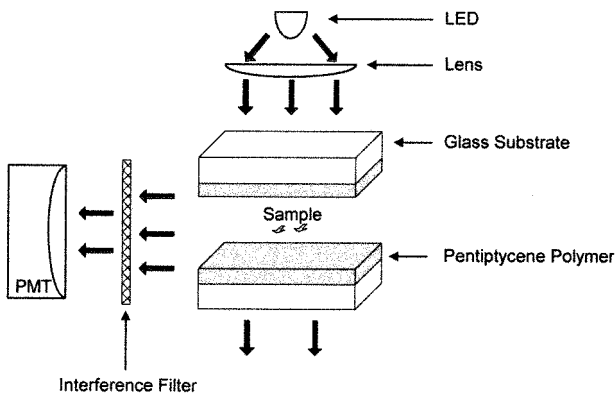


Fig. 5.   Schematic of sensor design.

that may contain target analytes is then drawn through the sampling chamber as the sensor inlet is held close to the ground and slowly swept across the area being interrogated. If the area contains nitroaromatic compounds, the intensity of the fluorescence registered by the PMT will decrease proportionally to the concentration of target analytes in the sample. If a decrease in fluorescence is detected, the operator is alerted to the possible presence of a landmine.

Fig. 6 illustrates the quenching response of the sensor to 100 picograms each of 1,3-DNB, 2,6-DNT, 2,4-DNT, and TNT separated and transferred to the sensor via a gas chromatograph. The gas chromatograph is used in our laboratory as a reproducible means of delivering quantifiable masses of ERCs to the sensor for calibration purposes. As can be seen from the figure, the sensor responds strongly to all four analytes at this level of mass loading. The response to TNT is approximately a factor of six greater than that to the DNT isomers. When not interfaced to the GC, the response of the sensor to the analyte is almost instantaneous upon sample introduction, indicating it is possible to detect landmines in near real time. 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 purge analyte from the films, returning the fluorescence intensity to near the initial baseline reading. Recovery times depend on several factors, the most important of which is the concentration of analyte in a positive sample. Typical recovery times after "hits" under field conditions are in the 5 to 10 s range for
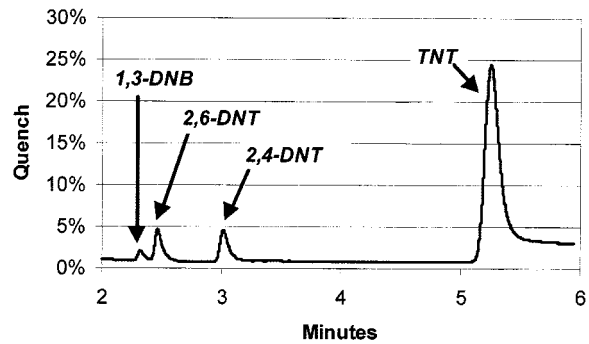


Fig. 6.   Sensor response to 100 picogram masses of several ERCs.

TNT, which recovers more slowly than other target analytes due to its stronger interaction with the films.

## V. Sensor Performance

### A. Laboratory Validation

The performance of FIDO was validated using gas chromatography with electron capture detection (GC/ECD). The ECD was selected for this purpose because it is one of the most sensitive laboratory detectors for explosives. Detection limits for TNT by ECD are in the 1–10 picogram range. Because the sensitivity of the ECD is orders of magnitude less than that of FIDO, sample preconcentration was necessary in order to analyze by GC/ECD the ERCs in some low-concentration FIDO test samples. Solid phase microextraction (SPME) was selected for this purpose [22]. The SPME sampling device contains a fused silica fiber coated with a sorbent coating. The fiber is mounted to a modified syringe that enables the fiber to be retracted inside a needle. This protects the fiber and prevents analyte uptake when it is not in use, and enables the fiber to be inserted through septa without damaging the fiber. To collect a sample, the coated fiber is inserted into the sample and is exposed to the sample for a specific length of time. When sampling ERCs by SPME, the mass uptake of analyte into the fiber is linear with respect to time over the dynamic range of the ECD (i.e., from approximately 10 picograms to 10 nanograms of sorbed ERCs) [6]. After sufficient exposure time to a given sample (determined by the time required to collect a mass of analyte within the dynamic range of the detector), the fiber is retracted inside the needle and is removed from the sample. For high concentration samples, the exposure time may be a few seconds, and for extremely low concentration samples of ERCs the exposure time may be several hours. The collected analyte is then usually desorbed from the fiber by inserting the retracted fiber into a heated block such as the injection port of a gas chromatograph. The fiber is then exposed inside the heated block, liberating the sorbed analyte for analysis. The uptake of ERCs is very temperature dependent, so samples are typically placed in a temperature-controlled bath during sampling.

Fig. 7 illustrates the response of FIDO to TNT in the headspace over a TNT-contaminated soil sample held in a glass bottle. To introduce the sample into the sensor, the lid was removed from the bottle followed by rapid insertion of the sensor inlet into the opening of the bottle. Sample was drawn from the headspace in the bottle at the rate of 1 ml/s
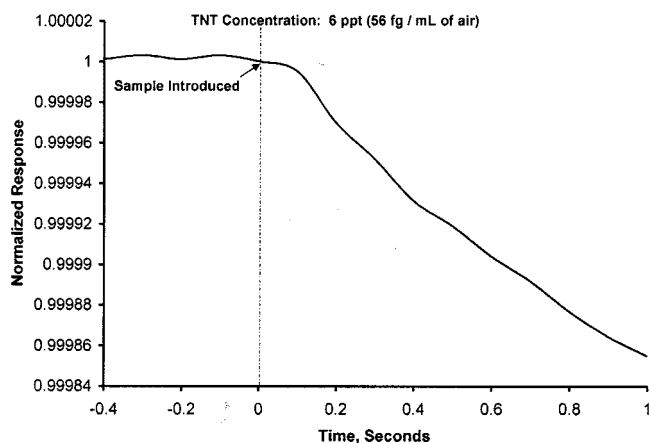
Fig. 7. FIDO response to 6 ppt of TNT in air.



Fig. 8. FIDO response to trace concentrations of TNT in the headspace over TNT-contaminated soils.

for a period of approximately 1 s. Stable baseline fluorescence can be seen before sample introduction, followed by a rapid reduction in fluorescence intensity as TNT vapor is drawn into the sensor. Prior to sampling the headspace in the bottle, the TNT headspace concentration in this sample was determined by SPME/GC/ECD. The concentration of TNT in the headspace over this sample was 56 femtograms of TNT/ml of air (six parts per trillion, n/n). The total analysis time by SPME/GC/ECD was 45 min, including a 20 min SPME sampling period. By comparison, FIDO was able to detect TNT in this sample almost immediately, and with no sample preconcentration.

A series of headspace samples from soils containing TNT was analyzed using FIDO. The soil samples were provided for analysis by Sandia National Laboratories, Albuquerque, NM, at the request of DARPA. The same series of soil headspaces was also analyzed by SPME/GC/ECD as previously described to determine the headspace TNT concentrations. This made it possible to determine the response of FIDO to soil headspaces containing a range of vapor-phase TNT concentrations. The concentration of TNT in the soil was also determined by elution of the TNT from the soil using acetonitrile as a solvent, followed by GC/ECD analysis of the extracts. The TNT concentrations in the soil ranged from 16–158/billion (mass/mass). Headspace TNT concentrations in these samples at 298 K ranged from 65 to 248 femtograms/ml of air. The headspace TNT concentrations were independently verified from duplicate samples analyzed at the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), Hanover, NH, and at Sandia National Laboratories. The response of FIDO as a function of soil headspace TNT concentration is plotted in Fig. 8. As can be seen from the plot, the response of FIDO exhibits good linearity over this concentration range. The minimum detection limit for TNT in these samples was placed at approximately 1 fg $(1 \times 10^{-15}$ grams) at an SNR of 3 : 1. This places the minimum detection limit of the sensor at approximately 1000 to 10 000 times less than that of the ECD.

Independent indoor validation of the sensor performance has also been performed at the DARPA test site at Ft. Leonard Wood, MO. Seventy-one soil and water samples were analyzed with FIDO. The samples consisted of 2,4-DNT in soil or water. The 2,4-DNT concentration in the sample headspaces was either 10 or 50 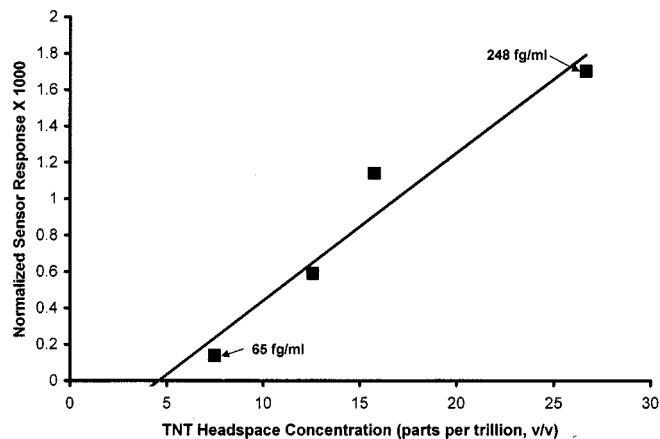ppb, or zero (a blank). The sensor easily differentiated blanks (some of which contained potential interferents) from samples containing 2,4-DNT. For the seventy-one samples analyzed, classification of the samples into each of the three groups (blank, 10, or 50 ppb) was made with no errors.

*B. Field Performance*

Blind field testing of FIDO against buried landmines has also been conducted at the DARPA test facility at Ft. Leonard Wood. Blind test lanes were established by marking potential target positions in the test field. At each test position, two flags were planted, approximately 50 cm apart. Some of the test locations were mined with the mine location centered between the flags and others were not. The landmines used for the test were authentic TMA5 or PMA1A landmines with the fuzes and detonators removed, with shipping plugs capping the detonator well. FIDO was used to sample between the flags at each test location. The sensor responses at each location were recorded and submitted to DARPA for scoring. In a lane consisting of TMA5 AT mines (plastic cased, containing TNT), the best sensor performance recorded was a probability of detection $(P_d)$ of 0.89, with a probability of false alarm $(P_{fa})$ of 0.27. Fig. 9 is a plot of probability of detection as a function of the probability of false alarm (a ROC curve) against targets in the blind AT mine lane.

Two experienced teams of canines, one trained to detect explosives, the other to detect landmines, were also present during the testing of FIDO. The team trained to detect explosives (i.e., bombs) withdrew from the test because of extreme difficulty in locating the mines. The team of canines with actual landmine detection experience in Bosnia and Mozambique performed much better, but the dog handler classified the field conditions as very difficult during the testing period. Specifically, the field conditions were very hot and dry, conditions under which the dog handlers stated that canine performance was typically poor. Both dog teams had extreme difficulty locating the landmines. At the end of testing, comparisons of FIDO performance were made to that of the dogs. Probabilities of detection and false alarm rates were in general better than that of the experienced canine landmine detection team. The performance of FIDO was verified by DARPA to be at a level equal to or better than that of the canines in the test. While the testing was limited
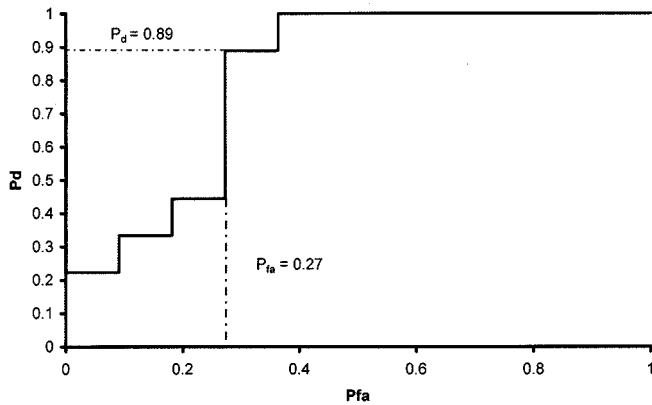
Fig. 9.   ROC curve for FIDO in the blind AT mine test lane at the DARPA landmine test facility, Fort Leaonard Wood, MO.

in scope, the performance of the sensor prototype was very promising. A report of the canine testing has been published elsewhere [9]. To the knowledge of the authors, this is the first time a chemical vapor "sniffer" has demonstrated the ability to detect landmines under field conditions with performance comparable to that of canines.

## VI. CONCLUSIONS

Detection of landmines by sensing chemical signature compounds in the air has been validated in field trials and laboratory tests administered by DARPA. The amplifying fluorescent polymer-based sensor prototype described here offers the potential of revolutionizing technology solutions for landmine detection, and offering extraordinary sensitivity and good selectivity to target analytes specific to landmines and UXO. Some improvements in the sensitivity and selectivity of the sensor have been made since the field tests described here. The sensor system is small (handheld), has low-power consumption (6 W nominal), is simple to operate, and production/manufacturing costs are anticipated to be relatively low. The sensing paradigm utilized may also be adaptable (through modification of the polymer structure) to field screening of other analytes including pesticides, chemical warfare agents, and other analytes of environmental interest. Investigations into other applications for this technology are underway.

## ACKNOWLEDGMENT

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