
ELECTROCHEMICAL METHODS (PAPER I)

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NEED TO DETECT A UNIQUE LANDMINE SIGNATURE

The detection of landmines has traditionally focused on secondary indicators that have given a high degree of false alarms. The classic technology that is still practiced is through the use of a metal detector. This was very effective in World War II, but, with the advent of landmines that are principally composed of plastic, the metal detector alarm needs to be set so low that for every 1 sq m of area checked, approximately 1.5 false positives are recorded. This has led to the extremely slow rate at which landmines can be removed, and a UN study reported that, at the present rate of removal, it will take over 1,000 years. In recognition of this problem, there has been a considerable effort put into such other detectors as ground-penetrating radar that alarm on density anomalies in the soil. The rationale for this approach is difficult to understand because soil generally has a heterogeneous composition and this method is unlikely to give a unique signal. Multiple other methods are being explored that seek

¹AUTHOR NOTE: I have been assigned to detail electrical and optical approaches to landmine detection. However, to place my analysis in the proper context, I have felt it important to describe some of the basic issues of specificity and the need to alarm on a unique chemical signature of a landmine. As such, my first section may serve a general role in discussing the pros and cons of direct explosive detection, as opposed to conventional approaches that use secondary signatures. Although the latter approach has been pursued for many years and has consumed the vast majority of the funding, it seems unlikely to ever work.

to detect thermal anomalies associated with the disruption of the soil by a landmine. Density and thermal anomalies may assist in freshly buried landmines and, in these cases, soil disruption may be visually apparent; however, they cannot be considered as reliable signatures for all landmines. Such approaches are more a result of researchers reconfiguring existing technology than searching for the best solution. The saying comes to mind, “If all you have is a hammer, everything looks like a nail.”

Focusing on secondary signals is flawed and gives a low degree of specificity and high false alarm rate. The continuing focus on these types of technologies is driven by the fact that the hardware exists, and they can have very fast response times. Although these technologies continue to advance slowly, with improved signal processing, new hardware, and fuzzy logic, the prospects for these technologies as an unambiguous indicator of landmines are low. The fact that this ground-penetrating radar only works in limited environments has led to restricted testing, and this practice was criticized by a recent General Accounting Office study [1].

The most reliable and rapid means to detect landmines is through trained canine-handler teams. Detailed research has shown that the dogs are indeed detecting the explosive vapor. As explosives are not naturally occurring materials, it is likely that they provide the most unique signature of a landmine. As a result, there has been considerable effort toward the detection of explosives in bulk or explosive vapors.

Two significant challenges face almost all chemical sensor technologies—sensitivity and selectivity. Landmine detection based on vapor methods presents daunting sensitivity requirements. The equilibrium vapor concentration of TNT, the principal explosive in landmines, is only 5–10 ppb. Vapor concentrations over a landmine, which are established by transport of the explosive compounds to the soil surface, are multiple orders of magnitude lower. (Tom Jenkins, whose work appears in Appendix Q, is an expert in this area.) DNT is a ubiquitous impurity in all explosives-grade TNT and because of its higher vapor pressure, detection of this analyte is also possible. Even higher sensitivity is necessary for rapid responses and the ability to sample a given suspected landmine location multiple times without depleting the small vapor headspace localized over the

site. Specificity is achieved when the molecular (chemical or physical) properties of the explosive are an integral part of the transduction process.

In assessing sensor technologies for landmine detection based on detection of the explosive, it is important to realize that reports claiming sensitivity to specific concentrations of explosives can be misleading. The low volatility of explosives makes it easy to concentrate these materials and hence even a low-sensitivity sensor may be able to detect explosives if exposed long enough. There is a limited amount of explosive in the soil and surface over a landmine, and hence it is most proper to refer to detection limits in terms of the number of molecules or mass.

ELECTRICAL TECHNOLOGIES

Detection principles based purely on electrical signals have advantages of being easily miniaturized and having low power requirements. The simplest method for detection is a change in the resistance of a transduction material. In general, semiconductive molecular solids and polymer films may have conductivities that are very sensitive to chemical vapors [2]. The general reason for this sensitivity is that the injected carriers in molecular and polymeric semiconductors are charged and electrostatic interactions of molecules result in trapping or untrapping of the carriers, thereby giving an increase or decrease in resistance. However, this inherent sensitivity also presents difficulties, and the sensor responses are generally variable based on the sample history, the morphology of the material, and the ionic impurities. More reliable sensors have been produced using inert intrinsically and electrically conducting particles of carbon dispersed in a swellable polymer [3]. The intrinsic low resistance of the particles causes them to be insensitive to electrostatic interactions. Molecular discrimination in this approach is the result of the relative solubilities of different molecules in the host polymer matrix. The specificity of individual sensors is very low and sensor selectivity is accomplished by constructing large arrays with a variety of host polymers. These types of sensor arrays are also known as artificial noses or electronic noses, and extensive measurements with different concentrations of analytes can be used to create algorithms that can be used to determine chemical

compositions of complex orders. These technologies have been examined for landmine detection, and sub-ppb detection limits for DNT over 5-second exposures have been claimed [4]. However, this technology suffers from two general limitations. The first is that the polymers must swell with the explosive, and this requirement generally leads to low sensitivity. Although this technology may be improved (i.e., nano-structuring), the detection of landmines in any conventional operational concept will require many orders of magnitude greater sensitivity. A second limitation is the fact that arrays having elements of low specificity leads to overlaps in the response to different chemical signals. In controlled laboratory environments, the arrays can be made to function; however, outdoor field tests with a large variable humidity prove to be problematic. Higher orthogonality between the responses of all of the different sensors in the array can solve this problem, but such an advance is unlikely based purely on solubility differences. There has been considerable interest recently in organic Field Effect Transistors, and these materials have been suggested as having potential as sensors [5]. This approach has better prospects for sensitivity; however, it will still likely suffer from the same lack of sensitivity.

Electrochemical methods have also been examined for the detection of explosives. This approach differs from the other electrical methods in that the measurement involved chemical modification of the explosives or their degradation products. An advantage of this approach is that the chemical properties of the signal, namely the potential at which an electron is injected or removed, provide some specificity. Electrochemical sensors can function to give a response in potential (voltametric) or current (amperometric). A fundamental requirement of electrochemical methods is the need for a mobile electrolyte to maintain charge balance once an electron is removed or injected into the chemical being detected. Most often this leads to systems that operate in a solution phase and hence explosives must be extracted from soil or extracted from vapors. Nitroaromatics, TNT and DNT, have a high electron affinity and may be reduced directly. The low reduction potential (high electron affinity) of TNT has been reported to provide a selective electrochemical means to detect low ppb levels of TNT in water [6]. Similar claims of selectivity based on the unique reduction potential have been suggested in different electrochemical devices and electrode materials [7].

Secondary products from explosives, generally nitrogen oxides (NO_x), can also be detected electrochemically. This has been accomplished by thermally decomposing the explosives bound to soil and detecting the gaseous NO_x products in amperometric sensors [8]. Nitro-groups can also be decomposed using the nitroreductase enzyme, and immobilized films with a conducting polymer for mediation with the electrode can be used to produce amperometric sensors capable of the detection of two micromolar concentrations of TNT and DNT [9].

Based on the limited sensitivity of conventional electrochemical sensors it appears unlikely that this is a viable technology for the detection of landmines. Additional considerations that also limit this technology are the need for mobile electrolyte and the fact that electrodes can be easily fouled. Conducting polymer coatings can help in the latter regard; however, this also introduces more complexity to the sensor.

OPTICAL DETECTION

Light of different wavelengths offers the chance to interrogate many different signatures that may be indicative of landmines. These range from infrared thermography to taking spectra of molecules.

Passive infrared imaging has been investigated in conjunction with other indirect methods in an attempt to increase selectivity through data fusion [10]. The interest in infrared solutions for landmine detection is likely related to the fact that there is an arsenal of Department of Defense knowledge in this area from the development of night-vision systems. The prospect that thermal anomalies over landmines, especially those that have been in the ground for extended periods, will be a robust indicator of landmines is extremely unlikely. Given the grave potential consequences of a system providing false negative readings, relying on this technique for detection rejection will never lead to an adequate discrimination.

There have been public claims of the ability of x-ray fluorescence for the detection of landmines. In this case the disclosed information has not held up to scientific scrutiny and appears to be principally intended to promote stock sales of a particular company [11].

In principle, spectroscopic techniques have the potential to provide the best selectivity for explosives. The infrared spectra of molecules can provide an information-rich fingerprint that allows for unambiguous identification. Direct detection by infrared absorption spectroscopy is not possible because of the limited sensitivity of this method. An alternative method with better sensitivity uses Surface Enhanced Resonance Raman Spectroscopy (SERRS), wherein light is scattered off an explosive molecule that is bound to a roughened highly polarizable silver or gold surface [12]. Although the SERRS method improves the sensitivity many orders of magnitude over conventional Raman Spectroscopy, this method still has insufficient sensitivity for landmine detection. In laboratory environments detection limits of 10^{-12} g of TNT were demonstrated and tests sponsored by the Defense Advanced Research Projects Agency systems could detect equilibrium vapor pressures of TNT (5 ppb) in 30 seconds. Hence, the sensitivity of this method is still multiple orders of magnitude too low.

Fluorescent methods are generally regarded as providing the highest sensitivity in conventional sensors. Hence there has been considerable interest in the detection of explosives by this technique. Fluorescence immunosensor displacement assays based on antibodies are widely used in biological sensing, and explosive detection systems have been developed on these principles. This method involves immobilization of TNT- or RDX-specific antibodies that are bound with a fluorescent label. Upon flowing a TNT or RDX solution over the antibody, the label is displaced by the explosive and a fluorescence signal is generated in the eluent phase [13]. Portable systems have demonstrated a 10 microgram per liter detection limit in water and this method has in principle very high selectivity and low detection limits. However, there are many factors that prevent this technology from being applicable to the landmine problem. The analysis in highly engineered systems [13] requires three minutes and prevents real-time landmine detection. Additionally, immunoassays have a number of limitations. The sensors must be kept at carefully regulated temperatures and are easily degraded or denatured in many chemical or thermal environments.

There have been multiple demonstrations of the direct detection of nitroaromatics by fluorescence quenching. The high electro-affinity of these compounds results in electron transfer from the excited

states of fluorescent molecules. Sensors utilizing this principle have been developed using small molecule [14] and polymeric fluorophores [15]. In the small molecule case [15], array sensors have been developed with 0.2-second response times and are capable of low ppb detection limits in a few seconds. The array nature of this sensor provides superior selectivity over a single element sensor. Given that the electronic nature of the nitroaromatics is necessary for a response this system tends to have better discriminating ability than the electronic noses previously discussed that utilized differential solubility in polymer hosts.

The most versatile and sensitive explosive sensors to date are based on electronic polymers [15]. These systems have the ability to create gain internally because of the ability of these materials to transport their excited states from one spot to another [16]. The high mobility of the excited states in these extended electronic structures allows the excited state to visit a number of potential binding sites prior to emitting light. As a result of this mobility, there is a much higher probability that the excited state will encounter a nitroaromatic and lower detection limits result. Prototype landmine detectors have been developed with 10^{-15} g sensitivity [17], greater than a factor of 103 better than other systems. The materials used in this device have been shown to have size exclusion properties that also improve selectivity [18]. This method of using energy transport in electronically extended systems appears to be general, and recent results using porous luminescent silicon also showed good sensitivity [19].

An important feature of fluorescence-based detection methods is the ability to detect landmines at a distance. By spreading special fluorescent sensory materials over a minefield, it should be possible to image the location of all of the landmines. Initial results support the fact that this technology has good potential as a standoff sensor [20].

There are a few other methods for optical detection of explosives, such as photofragmentation with deep ultraviolet laser light followed with the fluorescence detection of nitric oxide [21]. This method gave a detection limit of 40 ppb of TNT in soil. Optical absorption has also been investigated by using a cavity to increase the pathlength of the light through the explosive vapor [22]. Competition assays using surface plasmon resonance have also been developed, but these assays are not robust and lack sensitivity [23].

SUMMARY

The only robust primary indicator of a landmine is the explosive itself. There are many methods to detect explosives, however, most are limited by sensitivity and/or operational complexities. To date, only the fluorescence quenching method using amplifying electronic polymers has shown the necessary sensitivity in a portable device to detect landmines. This technique, in addition to allowing for hand-held prototypes, can be used in standoff detection methods.

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