
ELECTROCHEMICAL METHODS (PAPER II)*Thomas F. Jenkins and Alan D. Hewitt, U.S. Army ERDC-CRREL**Thomas A. Ranney, Science and Technology Corporation*

INTRODUCTION

Over the past several years, considerable resources have been expended to develop sensors capable of detecting buried landmines by sensing the vapors evolving through the soil and into the air above the mines. An effort was also made to characterize the vapor signatures of buried mines. This was done to provide the sensor developers with information on the qualitative and quantitative nature of the signature that is available for detection. Optimally, this second effort would have been completed first, providing specifications for the sensor community. This appendix addresses what is known about these signatures, their dependence on environmental constraints, and their implications for the probability of success of various chemical detection alternatives.

QUALITATIVE NATURE OF THE SIGNATURE OF BURIED MINES

The initial work on the qualitative nature of the chemical signature of buried mines was conducted in the late 1960s and early 1970s with the sponsorship of the U.S. Army Mobility Equipment Research and Development Center, Fort Belvoir, Va. The instrumentation used at that time was primitive compared with what is available now, but the conclusions of these studies are relevant. With respect to explosives-derived signatures, laboratory tests indicated that equilibrium vapor concentrations of 2,4-DNT generally exceeded that of 2,4,6-TNT by at least an order of magnitude for military-grade TNTs [1]. 2,4-DNT is a

manufacturing impurity in military-grade TNT and has been found to be present in most domestic and foreign TNTs [1,2]. For RDX (and Composition B), the most detectable vapor signature in laboratory tests was cyclohexanone, a solvent used in the manufacture of military-grade RDX [3]. Field tests indicated that cyclohexanone was detectable in the air above buried antitank landmines containing Composition B [4]. Composition B is composed of 60 percent RDX and 39 percent TNT.

In the more recent Defense Advanced Research Projects Agency (DARPA)-sponsored tests, chemical signature testing was limited to vapors that originated from military-grade explosives—largely TNT. Signatures attributable to other constituents of landmines, such as plastic casings, were not considered. Three samples of military-grade TNT were studied in depth: U.S. military-grade TNT obtained from Picatinny Arsenal, N.J., TNT taken from a Yugoslavian PMA-1A anti-personnel landmine, and TNT taken from a Yugoslavian PMA-2 anti-personnel landmine. Even though these TNTs were manufactured 35–55 years ago, 2,4-DNT and 1,3-DNB were the compounds detected at highest concentration in the vapor in equilibrium with the solid TNT [5]. 2,4,6-TNT was also detected in the vapor, but it was an order of magnitude lower in concentration.

The surfaces of four types of TNT-filled, Yugoslavian landmines (TMA-5, TMM1, PMA-1A, PMA-2) were sampled and in all cases the major signatures present were 2,4,6-TNT; 2,4-DNT; and 1,3-DNB. Often 2,4,6-TNT was the signature present at the highest concentration on the surfaces of these mines [6]. Similar results were found elsewhere [7]. These same mines were then buried at a research minefield at Fort Leonard Wood, Mo. Soil samples were collected and analyzed over the next three years to document the signature chemicals that accumulated in the surface and subsurface soils adjacent to these mines. Several thousand individual samples were collected and analyzed; the signature chemicals most often detected were 2,4-DNT; 2,4,6-TNT; and two environmental transformation compounds of 2,4,6-TNT, namely 2-amino-4,6-dinitrotoluene (2ADNT) and 4-amino-2,6-dinitrotoluene (4ADNT) [5,8].

Canadian researchers conducted a similar field study where seven different types of unfused landmines were buried in a gravel road. The soil was sampled three years after burial [9]. The same four sig-

nature chemicals (2,4-DNT; 2,4,6-TNT; 2ADNT; and 4ADNT) were found in these samples as found at the Fort Leonard Wood site.

Swedish scientists reported results from the analysis of soil samples collected in areas where various types of landmines had been excavated the previous week [10]. They reported the same suite of four signatures in soil samples from both a gravel road and deciduous forest. Soil samples were also analyzed from a Cambodian minefield. In these samples, only 2ADNT and 4ADNT were detected. From all these results, it appears that signature chemicals available in surface soils from TNT-filled landmines will largely be 2,4-DNT; 2,4,6-TNT; and its two transformation products, 2ADNT and 4ADNT.

FREQUENCY OF DETECTION AND ESTIMATE OF SURFACE SOIL CONCENTRATIONS OF MAJOR SIGNATURE CHEMICALS IN SURFACE SOILS

Thousands of soil samples have been analyzed at the U.S. and Canadian research minefields to estimate the concentrations of the four major signature chemicals in surface soils above buried mines. It is the concentrations of these signature chemicals in the surface soils and their air/soil partition coefficients that control the levels of vapor signatures in the stagnant boundary layer air over a buried mine.

Results from the Fort Leonard Wood and Canadian Forces Base Suffield indicate that the frequency of detection and the concentrations of signature chemicals vary tremendously from one type of landmine to another [5,9]. For example, the frequency of detection of TNT-related signatures in surface soils for TMA-5 antitank mines (plastic cased) was much greater than that for a TMM1 antitank mine (metal cased), even though they contained equivalent masses of TNT. This appears to be ascribable to the TMM1 being better sealed than the TMA-5 mine. Similarly, the frequency of detection of the PMA-1A antipersonnel mines was much greater than for the PMA-2 mines that appear to be hermetically sealed. Even for the TMA-5 and PMA-1A, though, detection (concentrations greater than 1 ppb) for the four signature chemicals varied from 11 to 33 percent for the individual signature chemicals during four sampling periods over 15 months. For both types of mines, the frequency of detection in-

creased in the order 2,4,6-TNT < 2,4-DNT < 2ADNT = 4ADNT. Median concentrations varied from about 44 and 17 ppb for 2ADNT and 4ADNT for surface soils over PMA-1A and TMA-5 mines, respectively, to 4 and 4 ppb for 2,4,6-TNT over PMA-1A and TMA-5 mines. Median concentrations of 2,4-DNT in surface soils were 32 and 16 ppb, respectively.

The relatively low concentrations of 2,4,6-TNT in these surface soils compared with the other signature chemicals appear to be attributable to a very short half-life for this compound. The half-life for TNT was estimated to be only about 1.1 days in Fort Leonard Wood soil at 22°C, whereas the half-life for 2,4-DNT was estimated at 26 days under identical conditions [11]. At Suffield, though, the mines were buried in a gravel road with apparently much less biological activity than at Fort Leonard Wood. The concentrations of 2ADNT and 4ADNT at Suffield were much lower relative to TNT than found at Fort Leonard Wood.

CONCENTRATIONS OF EXPLOSIVES-RELATED SIGNATURES IN THE AIR ABOVE BURIED MINES

Estimates of the concentrations of TNT-derived signatures in the boundary layer air above buried mines have been made on the basis of surface soil concentrations of signature chemicals and their partition coefficients [5, 12]. A series of soil samples was collected near buried mines at Fort Leonard Wood. The soils were subsampled and a portion analyzed to estimate soil concentrations of 2,4-DNT and 2,4,6-TNT. The remaining soils were enclosed in glass vials, and the headspace was allowed to come to equilibrium. This headspace simulated the boundary layer air above buried mines. The headspace was sampled using solid phase microextraction and was then analyzed. These results together with the soil concentrations allowed calculation of soil/air partition coefficients, which varied somewhat from samples to sample but were generally about of 10^5 for 2,4-DNT and 10^6 for 2,4,6-TNT. When these values were combined with median surface soil concentrations obtained for soils above PMA 1-A and TMA-5 landmines, estimates for vapor concentration of 2,4-DNT and 2,4,6-TNT were about 200 pg/L and 1 pg/L, respectively [5]. If we assume that about 10 mL of boundary layer air is available for detection, the mass of signature available for vapor sensors would be

about 2 pg for 2,4-DNT and 10 fg for 2,4,6-TNT. This assumes that all of the signature that is available could be collected. If we make an assumption that only about one-tenth of the available signature could be collected, then the mass of signature available would range from about 200 fg for 2,4-DNT to 1 fg for 2,4,6-TNT. Direct measurements of signatures in boundary layer air above buried mines at Fort Leonard Wood support these estimates.

Alternatively, if we could collect 1 g of surface soil particles for use in detection, the amount of signature chemicals available for detection would be about 20 ng for 2,4-DNT and 4 ng for TNT. This is an increase of 10^6 in signature mass for 2,4-DNT and about 4×10^7 for 2,4,6-TNT. Clearly this tremendous increase would translate into a much more reliable detection system. It also allows the use of low vapor pressure compounds like 2ADNT and 4ADNT for detection.

In another study, the soil/air partitioning behavior was examined in laboratory experiments, with particular emphasis on the dependence on soil moisture content [12]. These experiments indicated that the range of equilibrium vapor concentrations can be reduced as much as 10,000 for very dry soils, making direct vapor detection more difficult in arid areas. These results explain the positive results that we have found for improving the detection capability of vapor sensors by the use of surface watering.

RECOMMENDATIONS

The results discussed above, and the successful use of mine-sniffing dogs, clearly indicate that there is a chemical signature that can be used to detect the presence of buried mines. The source of the signature is surface soil contaminated from upward movement of signature chemicals. The nature of the explosives-related signatures has been characterized and is largely made up of four chemicals (2,4-DNT; 2,4,6-TNT; 2ADNT; and 4ADNT), the relative abundance of the four being dependent on the environmental conditions at the site. In some cases, for very poorly sealed landmines, the concentrations of these signatures in the surface soil can reach the ppm range, but more typically they are present in the low ppb range or below. While equilibrium between surface soil and boundary layer air is never really achieved, we can estimate the maximum concentration in the boundary layer air using an assumption of equilibrium. One must

remember, though, that the volume of boundary layer air available for detection is very small, perhaps in the tens of milliliters at most. The equilibrium in the boundary layer air is controlled by the soil/air partition coefficient that is highly dependent on the moisture content of the surface soil. Even in the most optimum case, this equilibrium is at least 10^5 , indicating that the signature available for detection is orders of magnitude higher in the surface soil particles than in the air. Most attempts to develop chemical sensors for mine detection assume that sufficient signature would be available in the air above the soil to enable detection. We believe that the concentration of signature in the air above the mine is too low and too dependent on environmental factors to provide a reliable target for detection. Surface soil particles, however, have much more signature present and the availability of this signature is less environmentally dependent. While it is less convenient to engineer a detection scheme based on the presence of this signature source, a sensor system based on contaminated soil particles will provide a much more reliable basis for detection. A system of this type was configured several years ago, but the sensor utilized at the time was not adequate [13]. Combining this approach with a sensor based on fluorescent-quenching polymers [14] is a concept that should be considered for future development.

When sensors were tested during the DARPA Dog's Nose Program, it was assumed that there was a signature to detect when sampling directly above buried mines. Results obtained near the end of this program, however, revealed that the location and magnitude of the signature can be offset from the mine depending on the slope of the ground in the vicinity of the mine [15]. It appears that this is because the movement of the signature is dependent on soil moisture movement, which creates a downslope plume. In recent tests, we have utilized an onsite analytical technique to verify the location of the surface soil signature before conducting vapor sampling [15]. One team of sensor developers was on site with us and indicated that this capability would be very valuable when testing sensors to verify that there is a signature present where the sensor was tested.

REFERENCES

1. D. C. Leggett, T. F. Jenkins, and R. P. Murrmann, *Composition of Vapors Evolved from Military TNT as Influenced by Temperature Solid Composition, Age, and Source*, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Special Report 77-16, 1977.
2. X. Zhao and J. Yinon, "Characterization of Origin Identification of 2,4,6-Trinitrotoluene Through Its By-Product Isomers by Liquid Chromatography-Atmospheric Pressure Ionization Mass Spectrometry," *Journal of Chromatography*, No. 946, 2002, pp. 125–132.
3. W. F. O'Reilly, T. F. Jenkins, R. P. Murrmann, D. C. Leggett, and R. Barrierra, *Exploratory Analysis of Vapor Impurities from TNT, RDX and Composition B*, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Special Report 194, 1973.
4. T. F. Jenkins, W. F. O'Reilly, R. P. Murrmann, and C. I. Collins, *Detection of Cyclohexanone in the Atmosphere Above Emplaced Antitank Mines*, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Special Report 203, 1974.
5. T. F. Jenkins, M. E. Walsh, P. H. Miyares, J. A. Kopczynski, T. A. Ranney, V. George, J. Pennington, and T. E. Berry, Jr., *Analysis of Explosives-Related Chemical Signatures in Soil Samples Collected Near Buried Land Mines*, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, ERDC TR-00-5, 2000.
6. V. George, T. F. Jenkins, D. C. Leggett, J. H. Cragin, J. Phelan, J. Oxley, and J. Pennington, "Progress on Determining the Vapor Signature of a Buried Landmine," in *Detection and Remediation Technologies for Mines and Minelike Targets IV*, A. C. Dubey, J. F. Harvey, J. Broach, and R. E. Dugan, eds., Seattle: International Society for Optical Engineering, 1999, pp. 258–269.
7. E. Bender, A. Hogan, D. Leggett, G. Miskolczy, and S. MacDonald, "Surface Contamination by TNT," *Journal of Forensic Science*, 1992, pp. 1673–1678.

8. V. George, T. F. Jenkins, J. M. Phelan, D. C. Leggett, J. Oxley, S. W. Webb, P. H. Miyares, J. H. Cragin, J. Smith, and T. E. Berry, "Progress on Determining the Vapor Signature of a Buried Landmine," in *Detection and Remediation Technologies for Mines and Minelike Targets V*, A. C. Dubey, J. F. Harvey, J. Broach, and R. E. Dugan, eds., Seattle: International Society for Optical Engineering, 2000, pp. 590–601.
9. S. Desilets, N. Gagnon, T. F. Jenkins, and M. E. Walsh, *Residual Explosives in Soils Coming from Buried Landmines*, Defence Research Establishment Valcartier, Technical Report DREV TR-2000-125, 2001.
10. A. H. Kjellstrom and L. M. Sarholm, "Analysis of TNT and Related Compounds in Vapor and Solid Phase in Different Types of Soil," in *Detection and Remediation Technologies for Mines and Minelike Targets V*, A. C. Dubey, J. F. Harvey, J. Broach, and R. E. Dugan, eds., Seattle: International Society for Optical Engineering, 2000, pp. 496–503.
11. P. H. Miyares, and T. F. Jenkins, *Estimating the Half-Lives of Key Components of the Chemical Vapor Signature of Land Mines*, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, ERDC/CRREL TR-00-17, 2000.
12. J. M. Phelan and J. L. Barnett, *Phase Partitioning of TNT and DNT in Soils*, Albuquerque, N.M.: Sandia National Laboratories, SAND2001-0310, 2001.
13. S. Desilets, L. V. Haley, and U. Thekkadath, "Trace Explosives Detection for Finding Landmines," in *Detection and Remediation Technologies for Mines and Minelike Targets III*, A. C. Dubey, J. F. Harvey, and J. Broach, eds., Seattle: International Society for Optical Engineering, 1998, pp. 441–452.
14. J. Yang and T. M. Swager, "Fluorescent Porous Polymer as TNT Chemosensors: Electronic and Structural Effects," *American Chemical Society*, No. 120, 1998, pp. 11864–11873.
15. A. D. Hewitt, T. F. Jenkins, and T. A. Ranney, *Field Gas Chromatography/Thermionic Detector for On-Site Determination of*

Explosives in Soils, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, ERDC/CRREL TR-01-9, 2001.