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Explosive Detection in the Marine Environment and On Land Using Ion Mobility Spectroscopy
A Summary of Field Tests

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A Summary of Field Tests

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ABSTRACT

Sandia National Laboratories has conducted research in chemical sensing and analysis of explosives for nearly 30 years. The objective of this work is to develop a field portable chemical sensing system that can be used to examine mine-like objects (MLO) and unexploded ordnance (UXO) in near-real time. Metal detectors, ground-penetrating radar, and other anomaly detectors can often locate suspicious objects, but cannot determine whether the devices contain explosives. Our focus has been on the classification of UXO in shallow water, unearthed mortar rounds and artillery shells, and anti-personnel/anti tank mines on land by sensing the low-level explosive signatures associated with these targets. The presence of explosive is, of course, the only truly unique characteristic of an explosive device. Three sampling subsystems have been designed; one for water collection, one for soil vapor sampling, and one for sampling exposed munitions. The water sampler utilizes a flow-through chamber that contains a solid phase microextraction (SPME) fiber that extracts and concentrates the explosive molecules. Explosive molecules are thermally desorbed from the concentrator into an ion-mobility spectrometer (IMS). The soil vapor sampler uses a soil probe (patent pending) that houses a SPME fiber. A low-flow air pump pulls soil gas across the SPME fiber for collection and concentration. The fiber is subsequently removed for analysis by ion mobility spectroscopy (IMS) or gas chromatographic analysis using an electron capture detector (ECD). The sampler for exposed munitions consists of a battery-powered pump and a short quartz tube. The gas flow is controlled such that explosive molecules adsorb onto the active sites on the quartz. Again, thermal desorption into an IMS removes the explosives and provides speciation. The chemical sensing systems are capable of sub-part-per-billion detection of TNT and related explosive compounds. This paper presents a descriptive overview of the results of several field tests. Supporting data are available by contacting the authors.

Acknowledgments

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INTRODUCTION

The detection of UXO and landmines has been a major concern for humanitarian demining programs, environmental remediation programs, and, in general, military organizations. The most common landmine and UXO detection methodology used today is the metal detector. This is a very sensitive technique, and can often detect the very small quantity of metal found in plastic cased landmines as well as deeply buried metal cased mines and UXOs. This technique, however, is not able to discriminate between a UXO or MLO and a piece of metallic litter, such as a shell fragment or old bottle caps. As a result, the false alarm rate associated with metal detectors is quite high.

Other systems, including sonar systems, ground penetrating radar, and other technologies are capable of detecting anomalies in the environment that may indicate the presence of UXO and MLOs. Many of these systems employ software algorithms that attempt to reduce the false alarm rate by distinguishing between munitions and naturally occurring items such as rocks. The success of these systems varies, and they have not been widely deployed in the field. This is often due to cost or difficulties of moving these oftentimes large and rather complex systems into the field. Again, a reduction in the false alarm rate would be highly desired.

The systems noted above are generally able to detect suspicious objects, but they do not utilize the one unique characteristic of mines and UXO – the presence of explosive molecules. Our current work has been focussing on the development of a small, portable detection system that can be used to determine whether there are explosive molecules associated with objects submerged in shallow water, exposed to the atmosphere, or buried on land in near-real time. Often, these objects will have been detected using other techniques, but by combining two different detection technologies, the false alarm rate can potentially be reduced to near zero. Our approach is to adapt and incorporate off-the-shelf technology to the greatest extent possible. Only a few basic detection instruments are available to be used in a chemical sensor system, whether the search is for objects in water or on land. We evaluated the available technology for application to this sensing system and determined the most practical instrument to be the ion mobility spectrometer (IMS). The IMS has the best balance of sensitivity and specificity available today. By specificity we mean that the IMS is capable of determining the identities of several explosive molecules in the same sample by isolating their signals. Although an IMS is not a quantitative instrument, it is capable of providing semi-quantitative data, and can be used to estimate the relative proportions of individual explosive compounds within the sample and to identify related degradation products as well. The IMS is sufficiently simple to operate, and the analyses may be reduced by microprocessor to a simple yes/no result. It is also adaptable to miniaturization and portable operation.

A major part of our research, which is required before one can apply any detection technology, is the determination of source concentrations, which we define as the signal strength. We have an ongoing research project directed at estimating this signal strength through the development of a mathematical model. The model is being validated by laboratory and field experiments. The calculated concentrations range from part-per-billion (ppb or $1:10^9$), to $1:10^{18}$ by mass. Similar estimates have been given by Spangler and Hogan, et.al.[1,2]. Field analyses have verified these estimates. A reasonable target concentration for a chemical sensor, therefore, seems to be about $1:10^{15}$. This concentration, whether in vapor or water, is several orders of magnitude less than the sensitivity of any currently available instruments that may be readily adapted to portable use. Therefore, it is necessary to enhance the signal by using concentration techniques before submitting the explosive analyte to the detection instrument.

ANALYSIS OF UXO IN THE MARINE ENVIRONMENT
Field Demonstrations

The process of detecting explosive signatures in water includes three basic steps. The first step involves sampling the water near a suspected target. The second step involves separating and concentrating the explosive molecules from the water and finally, the third step involves transferring the explosive analyte to a detector for processing.

We performed two tests using "staged" demonstrations where Sandia personnel placed known targets in the ocean. The first, performed on San Clemente Island off the coast of California, provided the first indication that the proposed approach to explosive detection was feasible. It also allowed researchers to obtain crucial data for subsequent testing. The second staged demonstration utilized live munitions placed in St. Andrews Bay, Panama City, FL. The third field demonstration was performed in Bedford Basin, Halifax, Nova Scotia, where UXO that had been submerged for over 50 years was successfully sampled and analyzed. These tests demonstrated the feasibility of using IMS as an explosives detector in the field. However, substantial work is still required for complete development of the technique.

San Clemente Island, CA tests

The first series of demonstrations at San Clémente Island, 1995-1997, consisted of placing a 55 gallon drum that was painted with mil-spec paint and contaminated with explosives (same average surface concentration as that found on the surface of sampled UXO) in approximately 45 feet of water. Divers were used to collect samples downcurrent from the drum using a hand-held sampling wand (Fig.1). A small pump on the surface drew water through the wand for collection and analysis on the surface (Fig 2), or from a stationary sampling manifold (Fig.3).

Figure 1. Diver using hand-held sampling wand.

Figure 3. Sampling manifold setup.

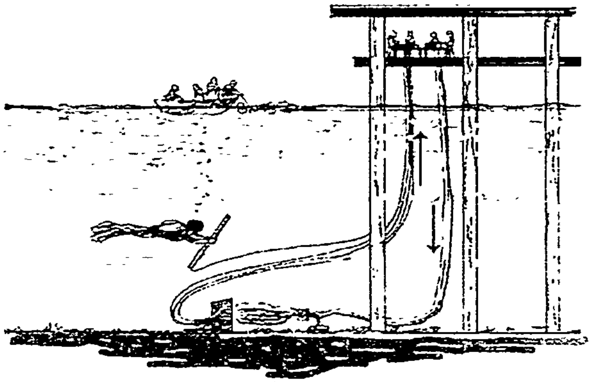


Figure 2. Field test setup at San Clemente Island.

Depending on the sampling scenario under test, between 1 liter and 100 liters of water were collected in amber jars. The explosives were extracted using extraction disks (3M Empore SDB-RPS) and the resultant extract analyzed on-site by IMS, with later laboratory confirmation by high performance liquid chromatography (HPLC).

The lessons learned during these San Clemente Island demonstrations, which took place during a three-year period were:

- Signal strength of the explosive decreases by an order of magnitude in the first meter downcurrent from the target, but then remains relatively constant for considerable distances. Small but measurable losses can be detected as a function of distance from the target. This large initial loss is believed to occur because of rapid initial adsorption of the explosive molecules onto suspended material in the water column.

After the initial adsorption, the active sites are satisfied, and additional concentration decreases can be attributed to diffusion in the water column.

- Explosive signatures could be obtained at distances greater than four feet from the target.
- Explosive signatures are released from targets for long periods of time. This testing was limited to several weeks, but later tests (Halifax, described below) showed that these signatures are present for many years.
- Explosives can be removed from the marine environment with good efficiency. The presence of marine organisms does not interfere with the extraction or analysis.
- Sampling and analysis procedures need to be improved. Sample collection and analysis required a minimum of three or four divers (safety requirement) and 3 to four analysts. Time required was > 2 hours.

Panama City, FL Tests

The second staged demonstration consisted of submerging live UXO (TNT fill) in St. Andrews Bay, Panama City, FL, September, 1998. During these tests, the water in St. Andrews Bay was very turbid. A hurricane that had passed through the area the previous weekend resulted in lots of suspended silt, and heavy rains produced significant runoff containing large amounts of tannin and other organic materials. For the tests, the UXOs were placed in 4 to 8 feet of water. Samples were taken by using a hand-held wand and a small pump to draw water past a SPME fiber. Personnel standing on a dock collected the samples. The UXO was not visible to the person collecting the samples, but a short tether constrained the sampling to within a 4-foot radius of the UXO. The sample collection / concentration system used for these tests is shown in Figures 4 and 5.

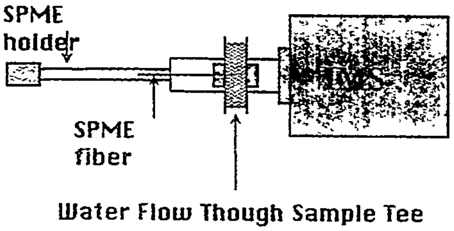
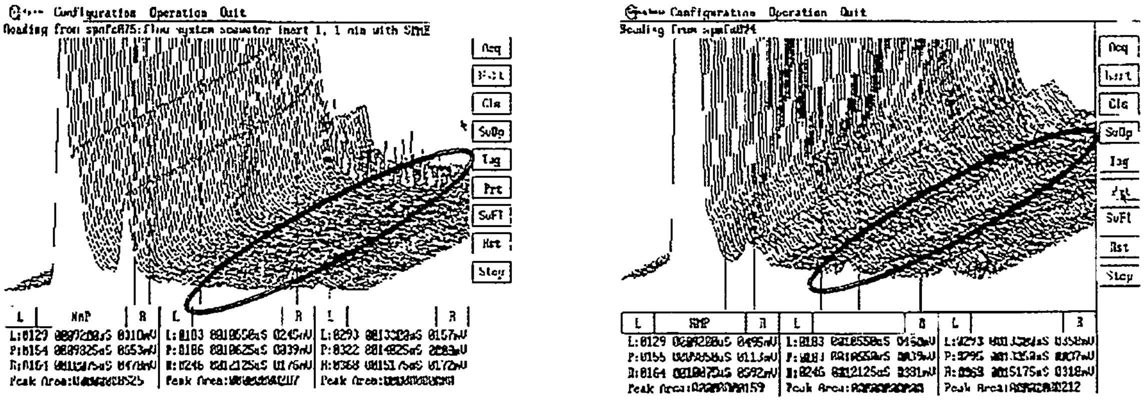


Fig. 4.. SPME / IMS concentrator / sampler schematic

Fig. 5. SPME / IMS system in fieldable configuration.

Using this system and a flow rate of one liter per minute, sufficient signals could be obtained with a two to five minute sampling time. Desorption of the SPME and analysis required less than one minute, making the total cycle time less than ten minutes. An example of the data collected using this system is shown in Figure 5a.



Inert target. No indication of explosive

Live target with explosive (TNT) signature.

Figure 5a. Example data from concentrator / IMS system.

The lessons learned during this Panama City demonstration, which took place over a five day period, were:

- Live UXO can be detected in the marine environment.
- Detection can be accomplished under adverse water conditions.
- Near-real-time sampling and analysis was demonstrated . Cycle time was less than 10 minutes (versus > 2 hours in the San Clemente tests).
- Personnel required for sample collection and analysis were reduced to two people. Divers may be required for some scenarios.
- Ten part-per-trillion calibration solutions (TNT) produced measurable signals using two minute sample collection times.
- Less than 1% collection efficiency was obtained using this test configuration. Nonetheless, sufficient sample was collected to obtain a definitive sensor response. The efficiency, which is a function of the ratio of the area of the SPME fiber to the cross section of the water flow path, as well as the flow rate past the SPME fiber, will be improved in the next generation collector.

Bedford Basin tests, Halifax, Nova Scotia

The final field demonstration in the marine environment was performed in Bedford Basin, Halifax, Nova Scotia, September, 1999. UXO that had been scattered in Bedford Basin as the result of explosions in 1917 and 1946 were sampled using a similar collector / concentrator / IMS system as was used in the Panama City tests. In Bedford Basin, however, movement of the boat precluded use of the IMS on-board ship. An IMS that is less sensitive to vibration than our research-grade IMS is currently being developed in our laboratory. Preliminary data indicates that the sensitivity of this system is comparable to the research grade system, and that it would be suitable for shipboard usage. SPME samples were collected using the interface shown in Fig. 6; the SPME fibers were then analyzed on-shore. Divers held the sampling wand near the UXO. Samples were collected at distances of 0.3 meters, 1 meter, 2 meters, and 3 meters downcurrent from the UXO, and at depths of 10 to 30 meters. Sediment samples were collected downcurrent at distances of 0.3 meters, 1 meter, 2 meters, and 3 meters. The UXOs sampled included 20mm small arms ammunition, 4" artillery shells (both fused and unfuzed), 5 inch artillery shells (both fused and unfuzed), 250 pound bombs, and samples taken near a beach contaminated with cordite (pelletized nitrocellulose doped with nitroglycerine and a petroleum "grease"). Figure 7 shows a diver collecting a sample near a 5-inch (diameter) projectile. Figure 8 shows a partially buried 4-inch shell. Note that in both cases, the targets are either fully exposed or only partially buried in sediment. No attempt was made to locate or sample fully buried targets. Marine growth was observed on most targets.

Fig. 6. Sample collection system, Bedford Basin

Figure 7. Sampling 5-inch shell with pump and hose to surface. Knife illustrates scale.

Fig. 8. 4-inch partially buried shell showing typical marine growth and amount of target exposed to the environment.

The lessons learned during the Bedford Basin demonstration, which took place over a ten day period were:

- UXO that has been submerged for 53 to 82 years often produces a detectable signature.
- 59 water samples were analyzed. 34 samples (58%) produced detectable explosives signatures. The number of live rounds actually present is not known at this time, so the accuracy of the analysis cannot be determined.
- 27 sediment samples were analyzed. 26 samples (96%) produced detectable explosives signals.

- TNT metabolites that are suspected to result from biological decomposition were present.
- Concentrations were observed to decrease with increasing distance from the target. Similar behavior was noted during the San Clemente Island tests.

ANALYSIS OF UXO EXPOSED TO THE ENVIRONMENT

Field Demonstrations

In July, 1998, Sandia personnel were asked to assist in determining whether mortar rounds that had been unearthed at the Massachusetts Military Reservation, Cape Cod, MA, were inert or contained explosives. The rounds, shown in Figure 9, showed a significant amount of corrosion. A total of 1,112 projectiles, including 60 mm mortars, 81 mm mortars, and 105 mm artillery shells were analyzed, along with 151 pieces of scrap ordnance, partial fuzes, and other items.

Fig. 9 Condition of mortar shells and partial view of sampling site.

The shells were analyzed by drawing air (100 ml/min) through a ¼ inch O.D. by 2 inch long quartz tube by using a small battery powered pump as shown in Figure 10. The samples were collected along seams, joints, and where breaches in the case could be observed.

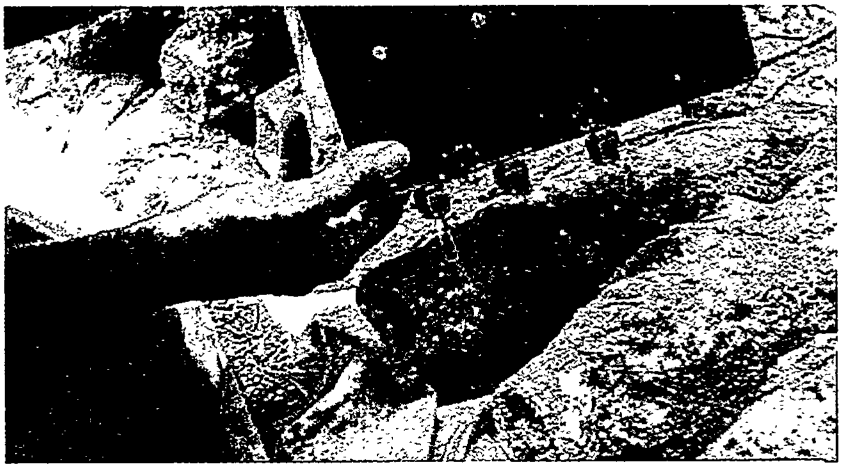


Fig. 10. Sampling pump being used to sample along seam.

Most shells were expected to contain inert filler, so to decrease the total sampling time required, the shells were analyzed in groups of 25. Sampling time was 125 seconds per group. One analyst collected the samples while a second performed the analysis. If a signal was observed, the shells in that grouping would be re-analyzed individually to determine which ones were producing the signature. In this manner, all 1,263 items were sampled in three days. Shells that appeared to be "different" than the rest (judgement call by the analysts) were sampled individually and for times up to 3 minutes per projectile. Typical responses obtained from these shells are illustrated in Fig. 11.

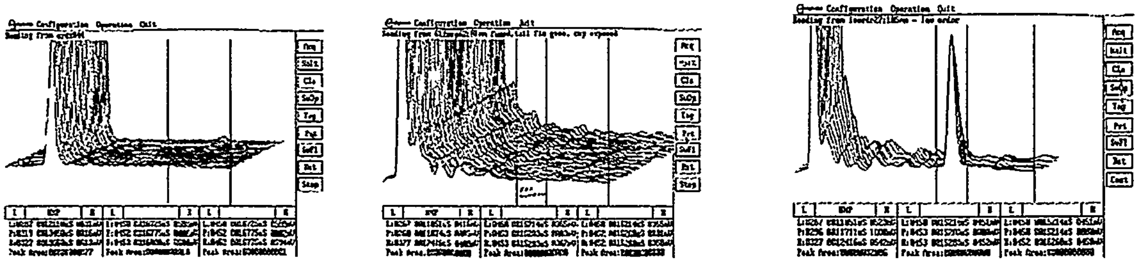


Fig. 11 Background signal, signal from inert round, RDX from live round.

Every shell was later cut open using a remotely operated saw to verify the contents. As expected, the vast majority of shells were found to be inert, both by the vapor sampling / IMS system and by cutting. Two intact 105 mm artillery shells were found to be live and were destroyed in place. No IMS signal was obtained from these rounds; the reason for this is not known at this time. A broken shell produced a signal attributable to RDX. No live mortar rounds were found.

Additional confirmation of the validity of this technique involved testing of ten 105 mm artillery shells at Sandia National Laboratories. These shells were believed to contain explosives. Each was sampled individually using the showing both TNT and RDX (Comp B fill). Postmortem analysis showed that the six rounds that produced a TNT signal contained a TNT fill. The other four rounds contained Comp B.

The lessons learned from these tests were:

- Large numbers of exposed UXO can be rapidly screened.
- Screening over 1200 items that were later demonstrated to be inert did not produce any false positives, but did produce two false negatives.
- Three 105mm artillery rounds were analyzed at Cape Cod. Two intact rounds did not produce an IMS signal, but did prove to be live. A round that had broken open produced a signal indicating RDX.
- Ten 105mm artillery shells analyzed at Sandia produced detectable signals. Six were correctly identified as having TNT fill; the other four were correctly identified as having Comp B fill.
- Additional work is required to obtain confidence limits for this type of analysis. Reasons for not obtaining a signal from two live rounds need to be determined.pump described above. Six rounds produced a signal indicating a TNT fill, and four produced signals

LANDMINE / BURIED UXO DETECTION
Field Demonstrations

The concept for the soil sampler was derived from field and laboratory experiments with explosive contaminated soil. A minefield was established at a Sandia Laboratories test site to determine the nature and quantity of the chemical (explosive) signature associated with buried landmines. A number of Soviet manufactured TM62-P anti-tank mines were obtained through the Office of Munitions for this experiment. These landmines are designed to be waterproof and can also be used as anti-landing mines in the ocean littoral zone. The mines were shipped unfuzed in their original wood packing crates.

It is assumed that the explosive signature flux from buried mines will be derived from two rates: short-term surface contamination, and long-term diffusion through plastic cases, seals, and gaskets. The quantity of initial explosive contamination on the mine surfaces was determined by swiping the surface with solvent moistened swabs. The results of these analyses are presented in Table 1 as nanograms (ng or 10^{-9} g) per square centimeter surface area. These data are in agreement with the range of values previously reported for mine surface contamination[3]. Following completion of the swipe tests, the unfuzed mines were buried at the test site.

Table 1. Surface contamination of TM62-P antitank mines analysis by gas chromatograph with electron capture detector.

Identity	Casing Material	TNT (ng/cm2)	2,4-DNT (ng/cm2)	RDX (ng/cm2)
AT-1	Bakelite	5.3	29	N.D.
AT-2	" "	10.2	28	N.D.
AT-3	" "	3.7	26	N.D.
AT-4	Polyethylene	4.3	6.4	5.1
AT-5	" "	2.9	1.5	7.8
AT-6	" "	2.3	7.7	11

The transport of chemical signatures through soil is affected by a number of environmental factors such as soil type and moisture content. A preliminary model of the chemical transport mechanisms has shown that there can be an appreciable time lag after a mine is buried before the vapor flux reaches the ground surface[4]. These studies have also shown that the majority of the chemical signature will be found adsorbed to soil particles. We allowed 150 days for the source "plume" to equilibrate with the soil above the mine before taking our first soil samples. Figure 12 shows the results of soil analyses taken from the vicinity of a buried landmine.

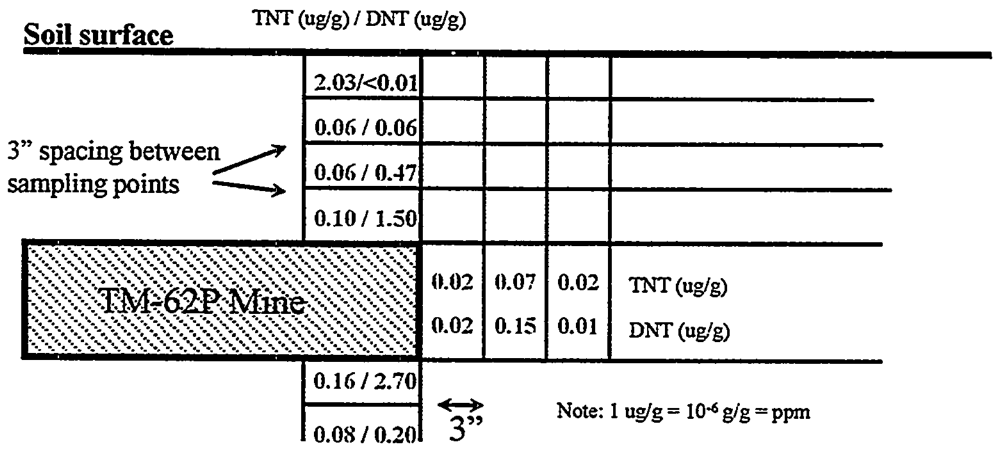


Fig. 12 Soil concentrations in vicinity of buried landmine.

The results of these analyses show that chemical signatures are detectable in the vicinity of buried landmines. These encouraging results prompted a series of experiments to determine the feasibility of extracting and detecting these signatures in the field.

Sandia researchers have developed a SPME analysis method to extract explosive compounds from soil samples by placing a SPME fiber in a holder that resembles a lawn dart. To confirm the presence of an explosive signature in the vicinity of a suspicious target the dart is inserted in the soil preferably within twelve inches of the target. If a larger area needs to be screened for the presence of explosives contamination or if individual objects have not been located, series of darts can be placed in an array. Dart placement and recovery can be by hand or remote deployment, and at depths from just below the surface to several feet down.

A small air pump is attached to the dart to draw vapor from the soil past the SPME fiber. Gas flows are restricted to less than 25 ml/minute to maintain the soil/vapor equilibrium in the immediate area of the target. This system is shown schematically in Figure 13. Figure 14 shows the field deployment of this system.

Laboratory and field experiments have shown that wetting the soil in the vicinity of a buried mine will increase the amount of vapor present such that the possibility of detection is enhanced. It appears that the addition of this water creates a “microenvironment” in which the explosive molecules are released from the soil particles, making them more available for adsorption onto the SPME fiber. The time of onset and duration of this ‘spike’ after the addition of the water is being explored in laboratory experiments.

After sufficient time has elapsed for concentration of the explosives, the probe is then retracted and the SPME fiber is thermally desorbed into an IMS or gas chromatograph. Alternatively, the SPME fiber can be solvent “stripped” and the analyte transferred to a liquid phase detector. Figure 15 shows the signature obtained from a Russian PMA-1A mine. This unit was analyzed by sampling 36 liters of soil gas. The SPME fiber was then thermally desorbed into a gas chromatograph equipped with an electron capture detector.

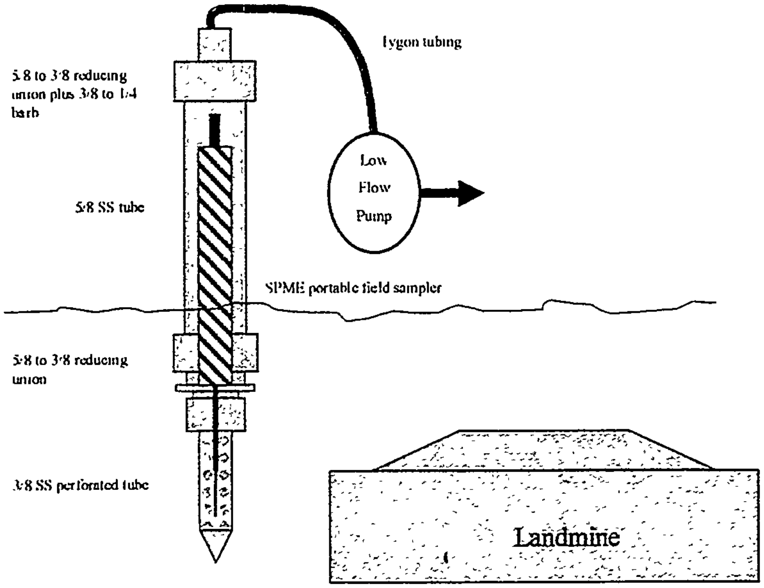


Fig. 13. SPME / lawn dart for landmine / UXO sampling

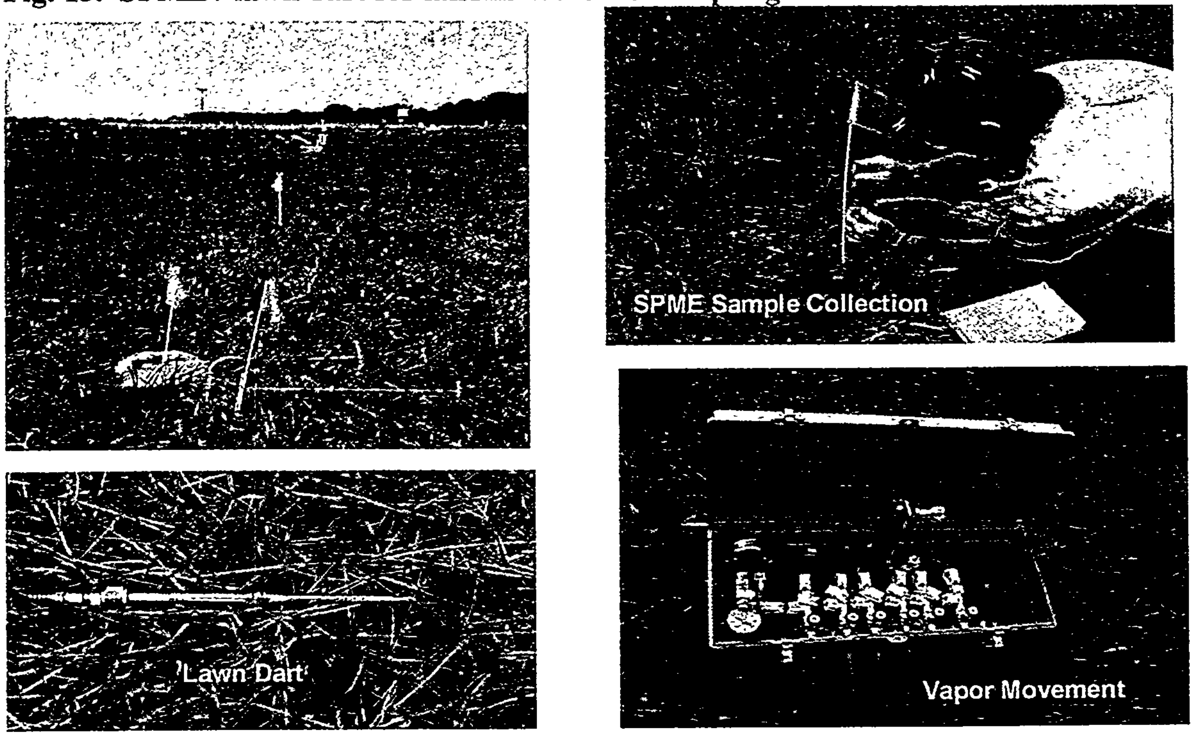


Figure 14. Lawn dart, SPME deployment, multi-station pumping system.

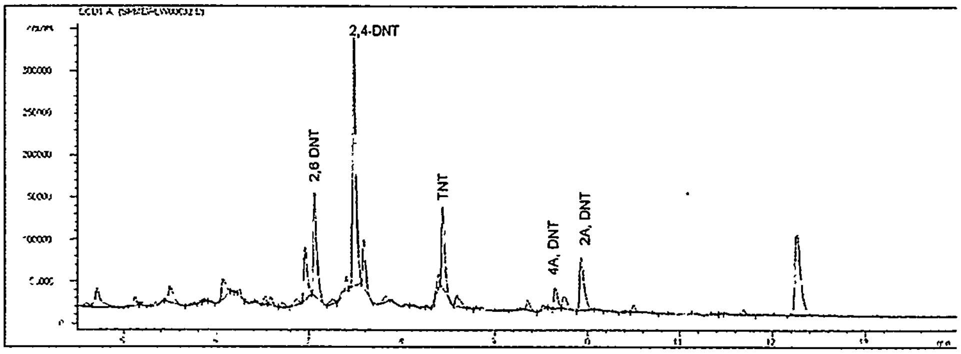


Fig. 15 Soil gas analysis of buried mine. Sampled using SPME / lawn dart; analyzed by GC/ECD

SUMMARY

Sandia has demonstrated the ability to collect, concentrate, and detect explosive molecules in water and soil at concentrations representative of buried or submerged explosive ordnance. The feasibility of classifying exposed munitions by collecting explosive molecules leaking through seals or seams in ordnance has been demonstrated. The base technology used for these demonstrations is commercially available hardware, adapted and modified for this purpose. Considerable work remains to be done in the design and integration of the various components to produce a field portable chemical detection system. A large part of the challenge stems from the fact that explosives exert very low vapor pressures and adsorb strongly to all surfaces. As a result, special purpose components that operate at elevated temperatures must be utilized to capture and deliver the explosive analyte to a detector. Additional work is needed to collect data and develop a database showing how much leakage would be expected from different types of UXO. Models predicting the movement of explosive molecules through various soils have been developed and validated using laboratory and field data. A thorough testing program to quantify the reliability of the techniques presented in this paper is required before this technology can be used in non-experimental situations.

Additional information can be obtained by contacting the authors.

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